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Role of cement content in determining resistance of concrete to reinforcement corrosion

Deshapriya, Medagoda Arachchige Ananda

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THESIS
2003.

ROLE OF CEMENT CONTENT IN DETERMINING RESISTANCE OF CONCRETE TO REINFORCEMENT CORROSION

by

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B. Sc. Eng. (Hons.)

A thesis presented in application for the Degree of Doctor of Philosophy

in the Concrete Technology Unit, University of Dundee,

Dundee, Scotland, UK

August 2003

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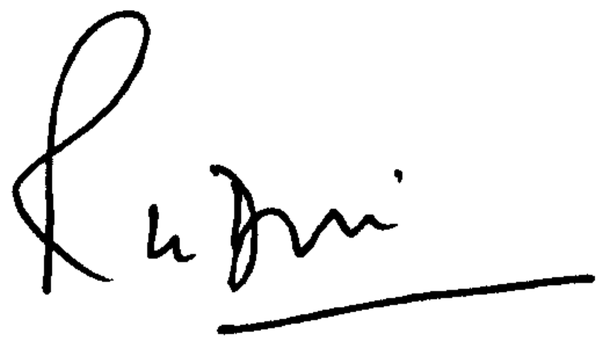
DECLARATION

I hereby declare that the following thesis has been composed by me, that the work of which it is a record has been carried out by myself, and that it has not been presented in any previous application for a higher degree.

Medagoda Arachchige Ananda Deshapriya

CERTIFICATE

This is to certify that Medagoda Arachchige Ananda Deshapriya has carried out this work under my supervision, and that he has fulfilled Ordinance 14 of the University of Dundee, so that he is qualified to submit the following thesis in application for the Degree of Doctor of Philosophy.



Professor R K Dhir

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ACKNOWLEDGEMENTS

The Author expresses his sincere gratitude to Professor R K Dhir, under whose supervision, this research was carried out, for his encouragement and advice throughout all phases of the project and great effort in supporting the Author's study.

Dr M J McCarthy is greatly acknowledged for his cordial advice and comments rendered to complete this research including write-up of this thesis. Many thanks are given to Dr P A J Tittle for his time, energy and guidance given in the first two years for planning, organising and carrying out of the project. The advice and comments given by Dr C Q Li, particularly to organise the Stage 3 of the experimental programme, are also greatly appreciated.

The financial support received from the Committee of Vice Chancellors and Principals of the Universities of the United Kingdom through the Overseas Research Students Award Scheme to cover a major part of the tuition fee is greatly acknowledged.

The support of research colleagues is also very much appreciated, particularly Mr S A Menzies for demonstrating many of the laboratory procedures and helpful discussions concerning the project. Thanks are extended to the technical staff of the Civil Engineering Department for their technical assistance ensuring the smooth running of the experimental work.

Finally, the Author greatly acknowledges the continuous moral support and encouragement of his family throughout his studies. This Thesis is dedicated to Author's late father who would have been so pleased to see the completion of his studies at the highest level and to mother.

ABSTRACT

Out of all the durability problems related to concrete structures, corrosion of reinforcing steel is the single most serious deteriorating process and this is likely to be more severe in the presence of defects (*e.g.* cracks) in the concrete surface. The review of published literature shows that at fixed w/c ratio, cement reduction is not mainly detrimental to fresh and hardened concrete properties and may improve performance in some cases. However, cement content variations (in some cases) are relatively small and do not cover an adequate range around the specified minimum cement contents in current standards. In addition, insufficient data exist to establish relationships between cement content and resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion. Moreover, no data were found on the combined influences of crack width and cement content on resistance of concrete to reinforcement corrosion.

Given this background, this study was designed to fill in many areas where information was either inconclusive or not available. The experimental programme, which was carried out in three stages, examined the influence of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the fresh, engineering, permeation, durability properties of concrete and, particularly, resistance of concrete (both cracked and uncracked) to reinforcement corrosion at the limits of specifications and beyond, covering concrete mixes made with a wide range of mix constituents.

Stage 1 of the study mainly showed that for a given set of mix constituents, at fixed w/c ratio, cement (and, therefore, water) reduction below the given minimum cement contents in current specifications did not adversely affect the fresh, engineering, permeation and durability properties of concrete. Indeed, many concrete properties were improved, particularly with the inclusion of limestone filler (with cement reduction) to maintain the mix fines content.

Stage 2 indicated that the observations noted for permeation properties were not influenced by aggregate or cement type. However, for a given mix, the resistance of concrete to permeation was improved by using lower absorption aggregates and PC / PFA or PC / GGBS, instead of PC. Cement reduction at fixed w/c ratio below the given minimum cement contents in current specifications had a minor adverse effect on the carbonation resistance of concrete, particularly when the fines content was allowed to deplete, and this was not influenced by aggregate or cement type. For a given mix, concrete containing lower absorption aggregate showed higher resistance to carbonation and that containing PC / PFA or PC / GGBS showed lower resistance. Furthermore, the effect of cement type on carbonation was more pronounced than that of cement content. However, cement content had no influence on the carbonation-induced reinforcement corrosion after initiation, regardless of aggregate and cement type. Moreover, the effect of cement content on corrosion rate was insignificant compared to the cement type and the use of PFA or GGBS with PC increased the corrosion rate compared to PC. Cement reduction at fixed w/c ratio below the given minimum cement contents in current specifications led to a reduction in chloride diffusion and chloride content, particularly with the inclusion of limestone filler to maintain the mix fines content, and this was not affected by aggregate or cement type. Again, for corresponding mixes, concrete made with lower absorption aggregate and PC / PFA or PC / GGBS showed greater chloride resistance. Furthermore, the effect of cement type on chloride diffusion was more pronounced than that of cement content. Reflecting the chloride resistance, cement reduction, particularly with the inclusion of limestone filler to maintain the mix fines content, improved the resistance of concrete to chloride-induced reinforcement corrosion, regardless of aggregate and cement type and, for a given mix, PC / PFA or PC / GGBS showed greater resistance compared to PC.

Stage 3 showed that for concrete with 0.3 mm surface crack (intersecting) width, cement reduction (below the specified minimum cement contents) at fixed w/c ratio slightly increased the chloride penetration through the cracked zone, but led to negligible influences on the resistance of concrete to chloride-induced reinforcement corrosion. Although there was a little influence of the surface crack (intersecting) width varying from 0.1 to 0.5 mm, on the chloride penetration through the cracked zones (not directly proportional to the width), it had no influence on chloride-induced reinforcement corrosion.

This study demonstrates that in most situations, there is no clear need to specify minimum cement contents and, if specified, their values should be reconsidered. Indeed, the minimum cement content may be an unnecessary restriction on mix design. Furthermore, if a reduced or no minimum cement is specified, attention should be made to specify a minimum fines content appropriately to achieve a closed structure and, consequently, to improve the performance of concrete. Moreover, it is a mistake to pay too much attention to cement content in determining the resistance of concrete to reinforcement corrosion, which is likely to be mainly influenced by cement type.

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ABBREVIATIONS AND TERMINOLOGY

TERM	DEFINITION
ACI	American Concrete Institute
A/C ratio	Aggregate / cement ratio by mass
Addition	Pozzolanic material, latent hydraulic material or limestone powder added to the concrete mixer as part of the cement content
Aggregate	Coarse aggregate, unless stated otherwise
ASTM	American Society for Testing and Materials
BSI	British Standards Institution
Cement	Portland cement (PC) alone or PC and one or more additions
CEN	European Committee for Standardisation
Filler	Very fine material used to adjust fines content, assumed to be inert (limestone powder in this study)
Fines	All particles < 75 μm, *i.e.* cement, filler (if used) and proportion of sand smaller than 75 μm
GGBS	Ground granulated blast-furnace slag
ITZ	Interfacial transition zone
Mix M1 (Reference Mix)	Concrete mix with average workability (75 mm nominal slump) with no superplasticizer
Mix M2	Cement-and-water-reduced (a 20 l/m^3 water reduction) mix with no filler
Mix M2*f*	Cement-and-water-reduced (a 20 l/m^3 water reduction) mix with filler
Mix M3	Cement-and-water-reduced (a 40 l/m^3 water reduction) mix with no filler
Mix M3*f*	Cement-and-water-reduced (a 40 l/m^3 water reduction) mix with filler
Mix M4	Plasticized reference mix with increased workability (180 mm nominal slump)
Mix M5	Cement-and-water-increased mix with increased workability (180 mm nominal slump)
PC, 42.5 N (or PC)	Portland cement with a strength class of 42.5 and a normal rate of strength gain
PFA	Pulverized-fuel ash
SP	Superplasticizer
SSD	Saturated surface dry
W/C ratio	Free water / cement ratio by mass

CHAPTER 1

INTRODUCTION

1.1 FIELD OF STUDY

Globally, concrete is the most widely used construction material (Wittmann *et al*, 1996), reflecting its versatility, economy, strength and, in most cases, durability. The last of these represents an area with which there has been mixed success and for which provisions are still developing. Indeed, inadequate material selection, poor mix design and experience of more severe environments than anticipated, are all factors that have contributed to difficulties in this area (CEB, 1989).

Since the early days, these issues have lead to a better understanding of the behaviour of concrete and a growing awareness of the significance of durability. Indeed, over the past 50 plus years, there has been significant development in the understanding of physical, chemical and mechanical deterioration under different exposure conditions. This has resulted in improvements in the classification of exposures as well as the introduction and development of limiting mix parameters in UK specifications, to ensure strength and durability of concrete structures for their intended working lives.

Traditionally, in many countries including the UK, for a given exposure class (anticipated environmental condition), concrete durability has been ensured by specifying three mix design limitations. They are;

- maximum free water / cement (w/c) ratio
- minimum strength grade
- minimum cement content.

In these specifications, as the severity of the expected environmental condition increases, the maximum w/c ratio decreases, and both minimum strength grade and minimum cement content increase. Whilst w/c ratio is linked directly to strength and, for a specific set of mix constituents, a reduction in w/c ratio improves most key aspects of concrete performance. Once the w/c ratio requirement is fulfilled, the minimum strength grade requirement ensures the proper material selection, *i.e.* it takes account of the range of cements and aggregates that may be used. However, the minimum cement content requirement to ensure durability of concrete is being increasingly questioned (Harrison, 1997; Concrete Society, 1999). Notably, a recent survey of concrete practice in fifteen European countries (Marsh, 1993a) indicated that minima varied considerably.

Furthermore, it revealed that some countries did not specify the minimum cement content requirement and, instead, relied on maximum w/c ratios and/or minimum strength grades.

If the w/c ratio and, consequently, the strength of concrete is kept constant, a decrease in cement content proportionally decreases the water content and hence the volume of cement paste. Therefore, the issue that needs to be addressed, once the specified maximum w/c ratio is set, is whether a reduction in cement content (hence volume of cement paste / hydrates) has any detrimental effect on concrete performance. At the same time, it should be noted that cement reduction at fixed w/c ratio requires the total aggregate content in concrete to be increased in maintaining yield and, therefore, the performance of concrete is likely to depend on both qualities of cement paste and aggregates. Furthermore, an increase in total aggregate content increases the aggregate-cement paste interfacial transition zone (ITZ), which is known to be the weakest part of the composite (Maso, 1996). Indeed, the combination of these different effects is complex. However, for a given exposure class, if cement reduction (at fixed w/c ratio) below the specified minimum cement contents in specifications is not detrimental to the performance of concrete, the minimum cement content requirement is possibly an unnecessary restriction on mix design.

On the other hand, it should be pointed out that until the development of very recent specifications, *e.g.* BS 8500: Part 1 (BSI, 2002), minimum cement contents specified in British codes of practice may have been used to control the w/c ratio (indirectly) rather than to ensure durability of concrete. This is because the minimum cement contents given in BS 8110: Part 1 (BSI, 1997) and BS 5328: Part 1 (BSI, 1997), appear to be calculated from the specified maximum w/c ratios and a nominal water content of 180 l/m^3, which gives medium workability for most aggregates available in UK when no superplasticizing admixtures are used (Teychenne *et al*, 1997). Thus, once the required maximum w/c ratio was set, the use of 180 l/m^3 water content (to control the workability) with calculated minimum cement contents provided a practical means of achieving it. Given this, it raises the question whether the minimum cement content is needed. This has even greater significance given the recent advances in concrete technology, including optimisation of particle packing in mixes (Dewar, 1999) and use of water-reducing and superplasticizing admixtures (Limbachyia, 1999) to enable acceptable workability to be achieved at water contents considerably below 180 l/m^3. Therefore, it may be possible to reduce cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, without adverse effect on concrete performance.

Furthermore, manufacturing of PC results in a greater environmental impact than producing of other constituent materials of concrete. This is mainly due to emission of carbon dioxide (CO_2) as a by-product of the PC manufacturing process. Indeed, it has been estimated that PC production contributes to approximately 7% of the world's man-made CO_2 emission (Malhotra, 2000).

Therefore, once the w/c ratio requirement is fulfilled, cement reduction below the specified minimum cement contents could reduce the environmental impact associated with concrete industry.

Given that there is little or no technical justification for minimum cement contents and possible beneficial effects of cement reduction at fixed w/c ratio, it highlights the importance of this research area, which has received little attention (Harrison, 1997).

Corrosion of steel in concrete is the single most serious deteriorating process in reinforced concrete structures (Dhir and Harrison, 1993). This is normally caused by the loss of alkalinity due to carbonation of concrete resulting in carbonation-induced corrosion, or by the presence of deleterious substances, particularly chlorides in solution around the steel resulting in chloride-induced corrosion. However, insufficient data exist to establish relationships between cement content and resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion (Harrison, 1997; Hobbs, 1998; Concrete Society, 1999). Therefore, there is the need to focus attention on the influence of variation in cement content at fixed w/c ratio on these aspects of performance.

Furthermore, in real-life, concrete structures undergo cracking due to physical, chemical, thermal factors and/or loading. These cracks are likely to permit greater migration of moisture, oxygen and aggressive agents through concrete, making the reinforcing steel more susceptible to corrosion (ACI Committee 224R, 1990; Stewart and Rosowsky, 1997). Moreover, no data were found in the literature review on the combined influences of crack width and variation in cement content at fixed w/c ratio on the resistance of concrete to reinforcement corrosion. Therefore, it is important to extend the study of role of cement content on the resistance of concrete to reinforcement corrosion to cracked concrete. This will establish the importance of concrete composition in the presence of a defect in the concrete cover. Indeed, it is important to consider cracked concrete with crack widths up to and beyond 0.3 mm, which is the maximum allowable crack width specified in BS 8110: Part 2 (BSI, 1985) for reinforced concrete structures in aggressive environments.

As mentioned earlier, cement reduction at fixed w/c ratio increases the coarse aggregate content, which is the highest single quantity material in concrete and, therefore, the performance of concrete possibly depends on the aggregate quality in addition to the quality of cement paste. Indeed, as the aggregate characteristics in the current specifications for concrete durability (BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002)) are often overlooked, it is useful to consider the combined influences of cement content and coarse aggregate characteristics in determining the performance of concrete.

1.2 AIMS AND OBJECTIVES

Given the background information above, the main aims and objectives of this investigation were to;

- review current knowledge on the influence of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio on the fresh, engineering, permeation, durability properties of concrete and its resistance to reinforcement corrosion
- examine each of these issues, particularly resistance of concrete (both cracked and uncracked) to reinforcement corrosion, at the limits of specifications and beyond, in a comprehensive experimental programme, covering mixes made with a wide range of mix constituents
- develop practical implications, based on the findings of the work, and guidance on concrete durability specification in practice.

1.3 SCOPE OF STUDY

The present investigation forms part of a wider overall project, which was carried out to investigate the variation in cement content at fixed w/c ratio on the performance of concrete. In the initial stage, Zhou (2001) focused on the role of cement content and coarse aggregate type (using concrete made with PC, 42.5 N and five coarse aggregate types, including lightweight aggregate), in determining the fresh, engineering, permeation and durability properties of concrete. Menzies (2002) examined the combined influences of cement content and type on the same concrete properties in the next stage of the project, using three of the most common cement types with natural gravel coarse aggregates. Further work was carried out by Karavasiliadou (1999), Masterton (1999), Brekos (2000) and Dignan (2000) to investigate the influence of cement content and type on the same properties using other PCs and binary / ternary cement combinations (all with natural gravel coarse aggregates). The current study is mainly concerned with the influence of cement content, cement type and aggregate type on the permeation characteristics of concrete and, more specifically, on resistance to reinforcement corrosion.

Initially, an extensive literature search was carried out to review the historical development of minimum cement content requirements in specifications, the background to carbonation-and-chloride-induced reinforcement corrosion in concrete and the published literature on the influence of variation in cement content at fixed w/c ratio on various aspects of the performance of concrete.

Thereafter, a comprehensive experimental programme was developed in three stages. For all these stages, a common approach was adopted to investigate the variation in cement content on a range of concrete properties. At a given w/c ratio, a series of mixes was designed and they were used selectively to test different concrete properties.

Initially, at a given w/c ratio, a Reference Mix was designed to have an average workability (a nominal slump of 75 mm) with no admixture. Its water content was governed by the characteristics of particular aggregate and cement types and was typically around 180 l/m^3. Thereafter, at fixed w/c ratio, cement content was reduced (thus, a water reduction up to 40 l/m^3) below the limits given in specifications and a number of other mixes were designed. Moreover, to investigate the effect of maintaining the fines content (particles < 75 μm) of concrete equal to that of the Reference Mix, with cement reduction, several other mixes were made with the inclusion of a limestone powder as part of the sand content. The workability of all cement-reduced mixes was maintained equal to that of the Reference Mix using a superplasticizing admixture. Furthermore, at a given w/c ratio, two other mixes were designed to examine the effect of increasing cement content (and hence a water content of typically up to about 200 l/m^3), giving higher workability (180 mm nominal slump), and the effect of raising workability from 75 to 180 mm nominal slump through the addition of superplasticizer, compared to the Reference Mix.

Given the importance of considering the combined influences of cement content and coarse aggregate characteristics in determining concrete performance, Stage 1 investigated the influence of cement content on the fresh, engineering, permeation and durability properties of concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate (the main cement and coarse aggregate type, used for the corrosion study).

Given that insufficient data exist to establish relationships between cement content and corrosion of steel in concrete (the single most serious durability problem), Stage 2 was carried out to examine the role of cement content, cement type and aggregate type on the resistance of uncracked concrete to carbonation-and-chloride-induced reinforcement corrosion using small-scale cube specimens. In addition, permeation properties of concrete (which influence the transport of aggressive substances, oxygen and moisture in concrete and hence the corrosion activity) and resistance of concrete to carbonation, chloride diffusion and chloride ingress (which indicates the effectiveness of the cover in preventing the corrosion process) were examined. The main cement type (PC, 42.5 N) was used with (i) natural gravel, (ii) granite and (iii) dolomitic magnesium limestone, and the main coarse aggregate type (dolomitic magnesium limestone) was combined with (i) 100% PC, (ii) 70% PC / 30% PFA and (iii) 50% PC / 50% GGBS, to ensure that the range of material properties and qualities currently in use, was covered.

As a simulation of real conditions of concrete structures, which undergo cracking, the influences of cement content and surface crack width, on the resistance of cracked (intersecting) concrete to chloride ingress and chloride-induced reinforcement corrosion, were investigated in Stage 3, using

concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate (using reinforced concrete beam specimens under static loading conditions).

Finally, based on the outcome of the experimental programme, the practical implications were examined in relation to specification of concrete for engineering design and durability.

1.4 OUTLINE OF THESIS

This thesis contains eight chapters. Chapter 2 covers the literature search, which is divided into three main sections. The first part reviews the historical development of minimum cement content requirements to ensure durability of concrete in UK specifications and the approaches towards minimum cement contents in other European countries and the USA. The second section covers the details of carbonation-and-chloride-induced reinforcement corrosion in cracked and uncracked concrete. Thirdly, it reviews the published literature dealing with the influence of variation in cement content at fixed w/c ratio on the performance of concrete.

Chapter 3 outlines the overall experimental programme of work, together with details of the materials, concrete mix design and mix proportions, specimen preparation and test procedures used during the investigation.

Chapters 4, 5, 6 and 7 present the findings of the experimental work. Chapter 4 considers the influence of variation in cement content at fixed w/c ratio on the fresh, engineering, permeation and durability properties of concrete. Chapter 5 deals with the effect of cement content on the resistance of concrete to carbonation-induced reinforcement corrosion. The role of cement content on the resistance of uncracked and cracked (intersecting) concrete to chloride-induced reinforcement corrosion is examined in Chapters 6 and 7, respectively.

Whilst each chapter includes a summary, Chapter 8 reviews the overall conclusions, practical implications of the findings for specification of concrete for engineering design and durability, and provides recommendations for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

As mentioned earlier, for a given exposure condition, concrete durability has traditionally been ensured by specifying an appropriate maximum w/c ratio, minimum strength grade and, in many countries including the UK, minimum cement content. The w/c ratio is linked directly to strength grade and, for a specific set of mix constituents, a reduction in w/c ratio improves most key aspects of concrete performance. However, the influence of minimum cement content requirements on concrete properties is being increasingly questioned (Harrison, 1997; Concrete Society, 1999). Indeed, insufficient data exist to establish relationships between cement content and durability, particularly the resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion (Harrison, 1997; Hobbs, 1998; Concrete Society, 1999).

Given this background, an extensive literature review was carried out to review existing knowledge on the influence of variation in cement content at fixed w/c ratio on a wide range of concrete properties.

Initially, the review considers the historical development of UK specifications for minimum cement content requirements to provide for the durability of concrete. Thereafter, it examines the approaches towards minimum cement contents in other European countries and the USA. It then, covers carbonation-and-chloride-induced reinforcement corrosion in concrete in detail. The final part of review examines current knowledge of the influence of variation in cement content at fixed w/c ratio on fresh, engineering, permeation and durability properties of concrete and resistance of concrete to reinforcement corrosion.

2.2 DEVELOPMENT OF MINIMUM CEMENT CONTENT WITH IN SPECIFICATIONS

2.2.1 UK Specifications

In the early part of the 20th Century, concrete mix proportions were specified by volume, for example, 1: 2: 4 ratio (cement: fine aggregate: coarse aggregate) was recommended by the Associated Portland Cement Manufacturers in 1921, without proper guidance on the water requirement. The British standards covering proportioning of concrete mixes were issued from the late 1940s. CP 114.100 (BSI, 1950, first issued in 1948), which covered normal reinforced concrete, recommended three mix proportions by volume for general use, namely 1: 1: 2, 1: $1^1/_2$: 3 and 1: 2: 4. These proportions would have given cement contents of about 275 kg/m^3 for the leanest

mix and 480 kg/m^3 for the richest. Maximum w/c ratios of 0.43, 0.51 and 0.58 were specified for these three mixes when uncrushed gravel was used. Again, there was little guidance on the control of the water content, although reference was made to the achievement of adequate workability. Only two environments ('internal' and 'exposed') were defined and, while different covers to reinforcement were specified for these, no reference to any other mix requirements was made. Surprisingly, when CP 114 (BSI, 1957) was revised, the inclusion of maximum w/c ratios was omitted. CP 115 (BSI, 1959) covering the use of prestressed concrete, both minimum and maximum cement contents were specified (approximately 290 and 525 kg/m^3, respectively). Again, no mention of maximum w/c ratio requirements was included, however, two minimum strength grades were introduced. As earlier, two exposure conditions were given and linked to the cover to reinforcement. In all of these codes, minimum cement contents and other mix parameters (if given) were not linked to different exposure classes and hence not directly to the durability of concrete.

CP 116 (BSI, 1965) for precast concrete, was the first British code to introduce a relationship between exposure conditions and required concrete grades. This defined three internal and six external exposure conditions (as there was some overlap between these, seven effective exposure conditions), and linked to both minimum strength grade (five, from approximately 20 to 50 N/mm^2) and minimum cover. Minimum cement contents of 240 and 300 kg/m^3 were specified for reinforced and prestressed concrete, respectively. A maximum cement content of 540 kg/m^3 was also specified. However, no values were given for water contents, although there was a requirement for accurate control.

In 1972, CP 114, 115 and 116 were replaced with a single code of practice for structural concrete, namely CP 110 (BSI, 1972). Five exposure conditions, namely 'mild', 'moderate', 'severe', 'very severe' and 'subject to de-icing salts', were introduced. For each condition, a minimum strength grade and a cover were specified. Minimum cement contents of between 250 and 360 kg/m^3, were specified for four of the five exposure conditions, with the 'very severe' exposure being included in 'severe'. The cement contents were related to the aggregate size and the type of concrete (reinforced, prestressed or plain). As with earlier codes, a maximum cement content of 540 kg/m^3 was also specified. In addition, maximum w/c ratios (linked to exposure) were introduced as an alternative approach and, if this property was strictly controlled, cement contents could be reduced by 20 or 30 kg/m^3.

During the 1980s, UK concrete designs and specifications have mainly followed BS 8110: Part 1 (BSI, 1985), which replaced CP 110. As before, there were five exposure conditions and, for each, maximum w/c ratio, minimum cement content, minimum concrete grade and nominal cover were given. Specified minimum cement contents were related to 20 mm nominal maximum aggregate

size and varied between 275 and 400 kg/m³ for reinforced concrete. An increase and decrease to the minimum cement contents were given for aggregate sizes smaller and greater than 20 mm, respectively (for example, 40 kg/m³ increase and 30 kg/m³ decrease, respectively for 10 and 40 mm nominal maximum aggregate sizes). In addition, it allowed reductions in cement content of up to 10% if the w/c ratio was significantly lower than the maximum specified, although another requirement was that percentage reduction in the w/c ratio should not be higher than that of the cement content.

A revised edition of BS 8110: Part 1 was published in 1997. Its durability requirements were in line with those of BS 5328: Part 1 (BSI, 1997), which introduced an additional (sixth) exposure condition, 'abrasive'. In BS 5328: Part 1, maximum w/c ratio, minimum cement content and minimum concrete grade were linked to exposure conditions, and the approach and the limiting values given were essentially very similar to those of BS 8100: Part 1 (BSI, 1985).

The new European standard, BS EN 206-1 (BSI, 2001) has recommended minimum cement contents (varying between 260 and 360 kg/m³), maximum w/c ratios and minimum concrete grades for eighteen exposure conditions. The limitations were related to an intended working life of 50 years. The draft complementary British standard to BS EN 206-1, BS 8500: Part 1 (BSI, 2002), which is due to replace BS 5328: Part 1 in December 2003, has similar requirements to BS EN 206-1. Indeed, it has sixteen exposure conditions if chemical attack is considered as a single class, which is however, further subdivided to cover a wider range of environmental actions in a different clause. Nominal cover is linked to exposure conditions and cement content is varied over a slightly wider range (between 240 and 400 kg/m³). In addition to the working life of 50 years, BS 8500: Part 1 gives mix limits for a 100-year working life (for selected exposure conditions).

Three other standards are worth mentioning. Firstly, for water-retaining structures, BS 8007 (BSI, 1987) refers to BS 8110: Part 1 and recommends a minimum cement content of 325 kg/m³, a maximum w/c ratio of 0.55 and a minimum strength grade of 35 N/mm^2. In addition, maximum allowable crack widths are related to exposure conditions.

BS 5400: Part 4 (BSI, 1990) specifies four exposure conditions for bridges and all are related to minimum strength grades, nominal covers and limiting crack widths. Minimum cement contents are also given in Part 8.

BS 6349: Part 1 (BSI, 2000) specifies minimum requirements for maritime concrete structures and gives two working life periods of 50 and 100 years, and is closely linked to BS EN 206-1 and BS 8500: Part 1.

Table 2.1 summarises the development of UK specifications for concrete durability. It is clear that over the past 50 plus years, there has been significant development in the understanding of concrete durability under different exposure conditions. This has resulted in improvements in the classification of exposures as well as introduction and development of limiting mix parameters.

Table 2.1 Summary of development of UK specifications
(Modified from Table 1 of Concrete Society (1999))

	1950, 1957 CP 114	1959 CP 115	1965 CP 116	1972 CP 110	1985 BS 8110	1997 BS 5328	2001 EN 206	2002 BS 8500
Exposure conditions	2	2	7	5	5	6	18	16[5]
Concrete grade linked to exposure conditions	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Minimum cement content linked to exposure conditions	No	No	No	Yes	Yes	Yes	Yes	Yes
Lowest minimum cement content (kg/m³)	275	290	315[1]	250[3]	275[3]	275[3]	260	240
Highest minimum cement content (kg/m³)	480	None	470[2]	360[3]	400[3]	400[3]	360	400
Maximum w/c ratio linked to exposure conditions	No	No	No	Yes	Yes	Yes	Yes	Yes
Cover linked to exposure conditions	Yes	Yes	Yes	Yes	Yes	No[4]	No[4]	Yes

[1] For 19 mm aggregate, medium slump, good control
[2] For 19 mm aggregate, medium slump, poor control
[3] May be reduced with good quality control
[4] Covers specified in appropriate design standard
[5] Chemical attack is considered as a single exposure condition

2.2.2 European Specifications

It is appropriate to consider how other European countries have dealt with concrete durability and, in particular, the use of minimum cement contents as most countries have developed their own specifications. Marsh (1993a) reviewed concrete practice in fifteen European countries, which revealed significant differences. The following section is a short summary based on the main review (Marsh, 1993b).

Table 2.2 summarises the ranges of durability requirements including minimum cement contents for various exposure classes for all CEN (members of the European Committee for Standardisation) countries. As expected, all European countries (except Belgium) specify

maximum w/c ratios, which are usually linked to exposure conditions. Notably, it is the only mix parameter for some exposure conditions in two countries (Norway and Sweden). As for British practice, thirteen countries (except Denmark and Sweden) specify minimum cement contents, although values are not quoted for all exposure conditions, and the minimum values vary considerably. Mostly, minimum cement contents are related to the maximum size of aggregate. Only five countries give minimum strength grade requirements (Denmark, Finland, Germany, Ireland and UK).

Table 2.2 Ranges of durability requirements for CEN countries
(From Table 1 of Marsh (1993b))

EXPOSURE CONDITIONS	MINIMUM COVER (mm)	MINIMUM CEMENT (kg/m^3)	MAXIMUM W/C RATIO	MINIMUM STRENGTH (N/mm^2)
Dry environment	5 - 20	0 - 280	0.65 – 0.90	20 - 30
Humid without frost	15 - 40	200 - 340	0.55 – 0.90	15 - 35
Humid with frost	15 - 40	200 - 380	0.55 – 0.60	25 - 40
Humid with frost and de-icing salts	25 - 40	200 - 380	0.45 – 0.55	25 - 40
Sea water without frost	25 - 45	200 - 340	0.45 – 0.55	24 - 40
Sea water with frost	25 - 45	200 - 380	0.45 – 0.55	25 - 40
Chemical aggressiveness:				
Slight	20 - 45	270 - 340	0.45 – 0.60	25 - 35
Moderate	20 - 45	270 - 385	0.45 – 0.50	25 - 35
High	20 - 45	270 - 385	0.35 – 0.50	35 - 40

2.2.3 American Specifications

Generally, American specifications (ACI Committee 201.2R, 1992; ACI Committee 301, 1999; ACI Committee 318/318R, 1999; ACI Committee 345R, 1991) specify maximum w/c ratios and minimum strength grades for a range of exposure conditions. In addition, minimum air contents are also given for freeze / thaw environments. However, it should be noted that minimum cement contents are specified in the codes, for example, 330 kg/m^3 for bridge decks and 320 kg/m^3 for floors (for nominal maximum aggregate size of ¾") to ensure workmanship rather than durability.

2.3 CORROSION OF STEEL IN CONCRETE

2.3.1 Corrosion Process

Protection Provided by Concrete to Steel

Corrosion of steel in concrete is one of the major causes of deterioration in reinforced concrete structures (Neville, 1995) and, possibly, the most serious durability issue (Mangat and Molloy, 1992). Concrete normally provides excellent corrosion protection to embedded steel by both chemical and physical means (ACI Committee 222R, 1996). In addition, the electrolytic resistivity of concrete also has a decisive influence on the behaviour of steel when conditions are such that corrosion may occur (Page, 1985; Millard, 1991).

The chemical protection is mainly associated with the highly alkaline environment in the concrete. The alkaline environment within the concrete pore fluid is generally attributed to the calcium hydroxide, which is the by-product of the hydration of dicalcium and tricalcium silicate (C_3S and C_2S) compounds in Portland cement. In addition, soluble alkali metal oxides present in the cement form hydroxides when water is added, further increasing alkalinity and causing the pH of the concrete pore water to be in excess of 12.5 (CEB, 1989; ACI Committee 222R, 1996; Concrete Society, 2000). In these conditions, a tightly adhering, very thin, dense, self-renewable oxide layer is formed on the surface of the steel which protects the steel from corrosion and is referred to as a passive layer (Gonzalez *et al*, 1996; Concrete Society, 2000). The precise composition of the passive layer is not clearly understood (Broomfield, 1997) and is referred to as γ-Fe_2O_3 (γ-ferric oxide) (Pourbaix, 1976; Neville, 1995).

The physical protection against corrosion is provided by the concrete cover, which acts as a barrier to the penetration of aggressive agents in liquid or gaseous form through its pores. The less permeable and greater the concrete cover depth, the longer will be the time to corrosion and service life of the structure concerned (Tuutti, 1982). The main factors governing the quality of the concrete cover and hence the resistance to penetration of aggressive agents, are w/c ratio, compaction and curing (CEB, 1989).

Corrosion Initiation and Propagation

Corrosion of reinforcing steel in concrete is normally caused by one of the following phenomenon;

- the loss of alkalinity due to carbonation of concrete
- the presence of deleterious substances, particularly chlorides in solution around the steel.

As highlighted above, these are normally the result of ingress of agents from the environment. Problems normally occur once these substances have passed through the concrete cover and have

reached reinforcement sites (in sufficient quantities, in the case of chloride), and corrosion is initiated.

During the propagation stage, reinforcement corrodes, the rate of which depends on a number of factors, causing loss of metal and/or loss of bond, both leading to a loss of structural capacity. In addition, the increased volume of corrosion products results in cracking, spalling or delamination of concrete, which may further accelerate ingress and damage (Neville, 1995).

This deterioration process can be graphically represented by the model proposed by Tuutti (1982), see Figure 2.1.

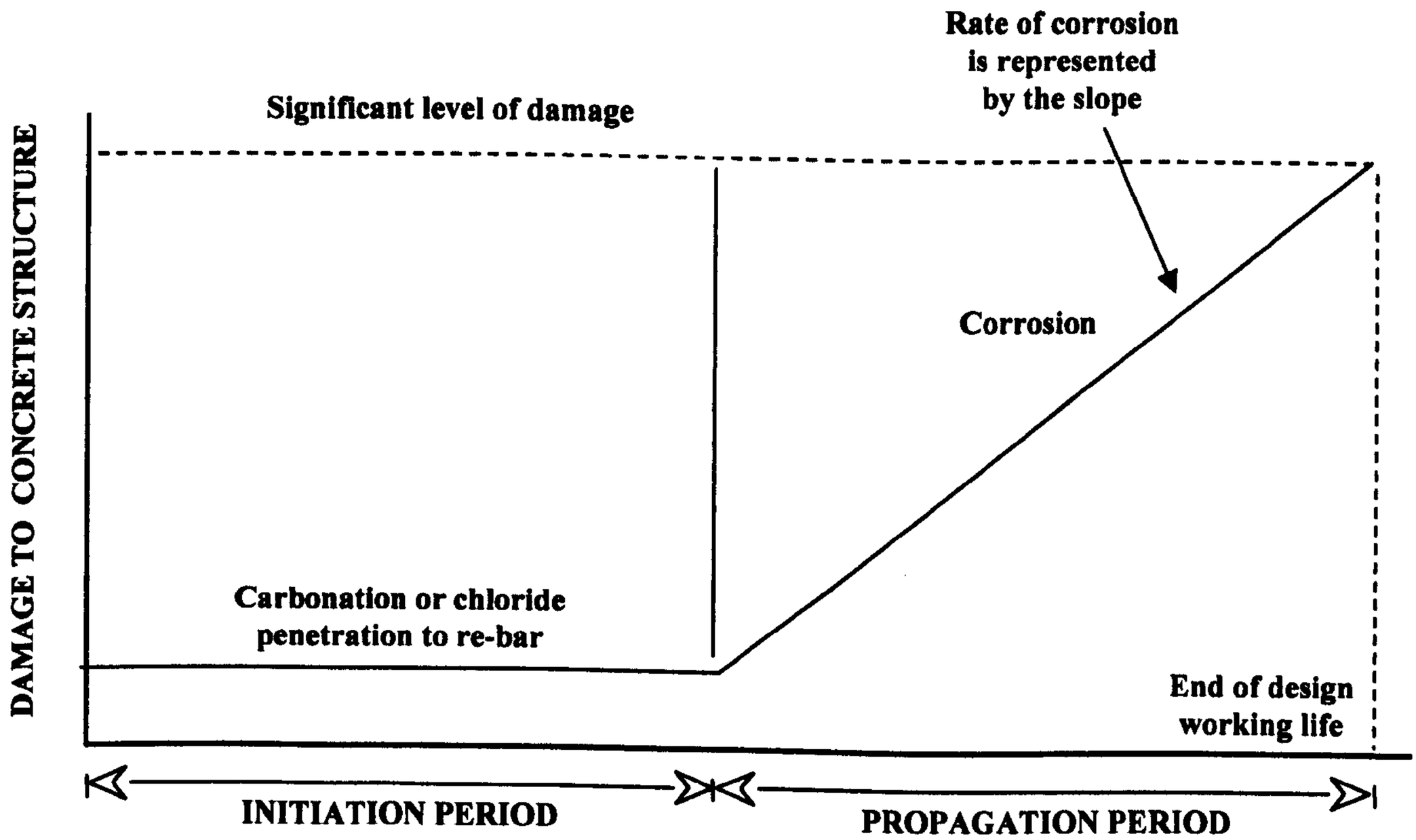


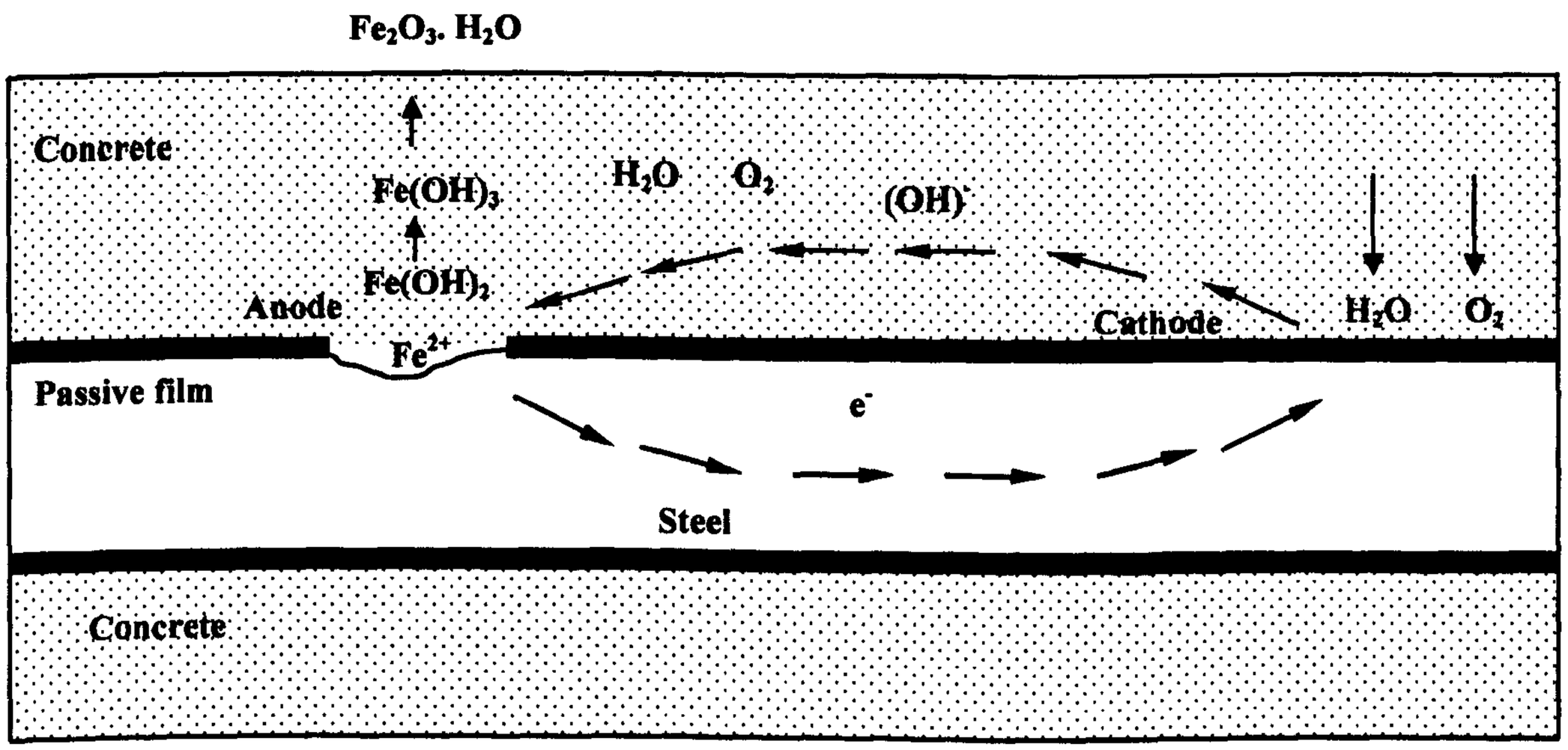
Figure 2.1 Model of corrosion of steel in concrete proposed by Tuutti (1982)

This represents the deterioration process against time. There is some disagreement on what may be considered to be an allowable level of damage during the propagation period and a number of conditions have been proposed as follows (Concrete Society, 1996);

- no corrosion permitted
- first cracking (visible with magnification)
- cracking visible to naked eye (a surface crack width of about 0.1 to 0.2 mm)
- first spalling
- excessive deflection
- collapse under the design loading.

Mechanism of Corrosion

Although iron can corrode by chemical attack, the most common form of corrosion in an aqueous medium is electrochemical (ACI Committee 222R, 1996). Once the passive layer breaks down, steel in concrete corrodes making positively charged ferrous ions (Fe^{2+}) and negatively charged free electrons (e^-), which is the anodic reaction. The surplus electrons in the steel combine at the cathode with water (H_2O) and dissolved oxygen (O_2) to form hydroxyl ions (OH^-), the pore water in the hardened cement paste providing the electrolyte. The hydroxyl ions combine with the ferrous ions to form ferric hydroxide ($Fe(OH)_3$), which is converted by further oxidation into rust. A schematic representation of electrochemical corrosion is shown in Figure 2.2. It is to be noted that the hydroxyl ions generated in the cathodic reaction increase the local alkalinity and, therefore, strengthen the passive layer, thereby inhibiting the effects of carbonation and chloride ions at the cathode (Broomfield, 1997).



Anodic Reactions

$Fe \rightarrow Fe^{2+} + 2e^-$

$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2$ (ferrous hydroxide)

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ (ferric hydroxide)

$2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O$ (hydrated ferric oxide or rust)

Cathodic Reaction

$4e^- + O_2 + 2H_2O \rightarrow 4(OH)^-$

Figure 2.2 Schematic representation of electrochemical corrosion

It can be seen that oxygen is consumed at the cathode and water is regenerated. Both are essential for the corrosion process to occur. Thus, no corrosion takes place in either a dry concrete (where the electrolytic process is impeded) or in a water-saturated concrete (where oxygen cannot

penetrate), even if the passive layer has been destroyed (CEB, 1989). Once the passivity is destroyed, the highest corrosion rate occurs in concrete surface layers subjected to highly changing wetting and drying conditions (CEB, 1989; Mehta, 1991; ACI Committee 222R, 1996; Stewart and Rosowsky, 1997).

Hydrated rust has a substantially higher volume than steel and it is more porous. Depending on oxygen availability and hydration, the volume increase at the steel / concrete interface is several times the original steel (Broomfield, 1997). This leads to splitting forces that cause cracking, spalling or delamination of concrete (see Figure 2.3), as mentioned earlier.

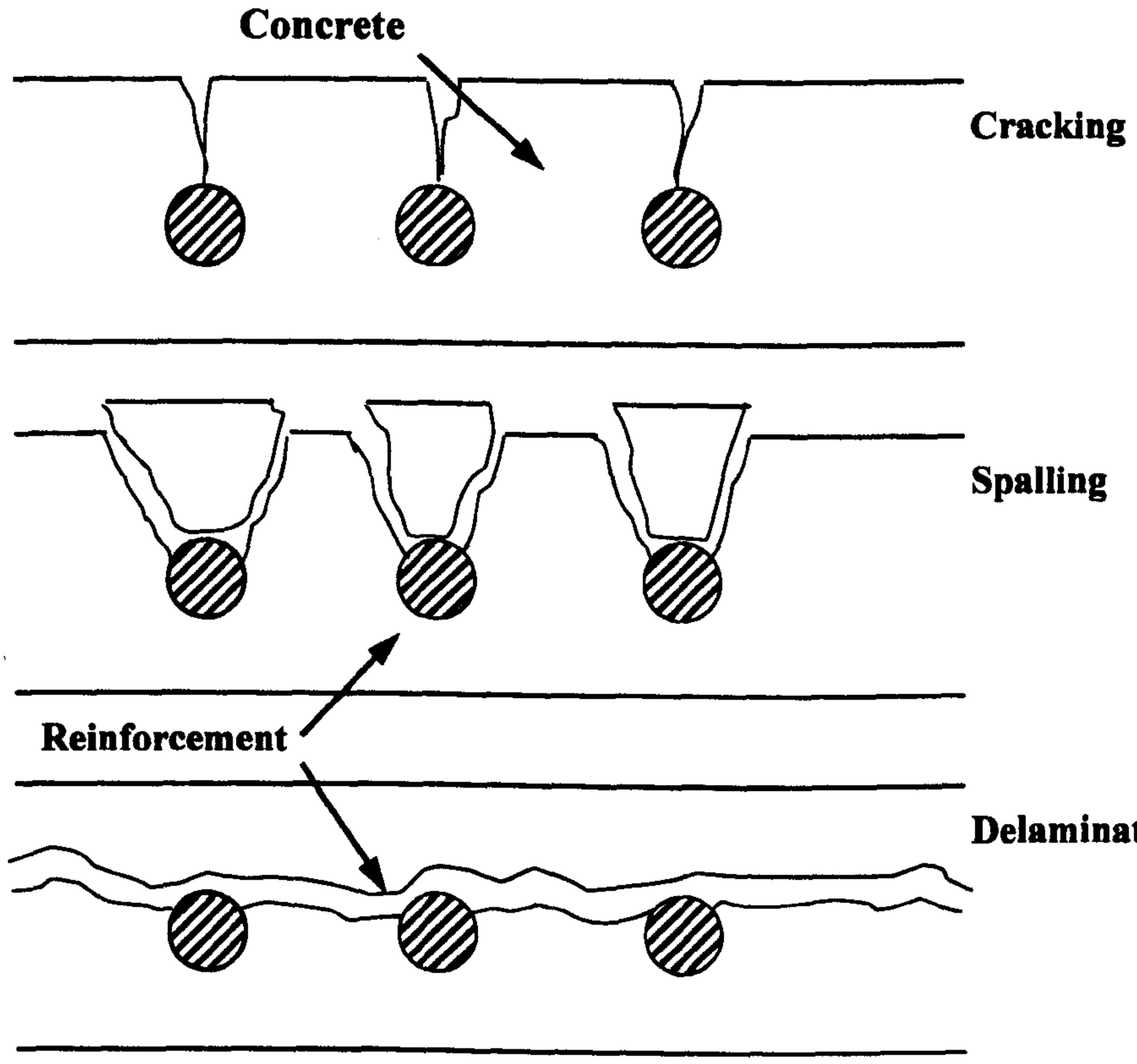


Figure 2.3 Diagrammatic representation of damage due to corrosion (Neville, 1995)

2.3.2 Carbonation-Induced Corrosion

Carbonation Process

Carbon dioxide (CO_2) gas in the atmosphere, on average 0.04% by volume, diffuses into concrete and, in the presence of moisture, chemically reacts with the alkaline hydroxides in concrete, and is referred to as carbonation. The chemical reactions occurring can be described as;

$$CO_2 + 2H_2O \rightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$H_2CO_3 + Ca(OH)_2 \text{ (calcium hydroxide in pore solution)} \rightarrow CaCO_3 \text{ (calcium carbonate)} + 2H_2O.$$

Bennison (1984) and Dhir *et al* (1992) state that the sodium and potassium hydroxides in the concrete can also react in a similar way to the calcium hydroxide, resulting carbonates.

The reduced alkalinity accompanying the reactions leads to the passive conditions in which embedded steel exists to be destroyed. There is some uncertainty as to the extent of the reduction in alkalinity, but the pH of carbonated concrete is considered to be around 8.0 (Parrott, 1987). Normally, there is a rapid transition between the highly alkaline and the neutralized regions (Parrott, 1987). Therefore, a sharp reduction in pH occurs over a narrow concrete depth, separating carbonated and non-carbonated regions.

Mechanisms of Carbonation Transport

The carbonation front advances at a decreasing rate because carbon dioxide has to diffuse through the pore system including the already carbonated surface zone of concrete (Neville, 1995). The rate of movement at steady hygrometric conditions approximates to Fick's second law of diffusion. Thus, it is possible to relate the carbonation depth (d) to time (t), as given below.

$$d = \text{constant} \times \sqrt{t}$$

However, as the carbonation process proceeds, it modifies the pore structure and the concrete composition. These changes and varying moisture levels with depth lead to deviation from the idealised diffusion equation (Broomfield, 1997). Empirically, a number of equations have been used to link the carbonation rate, the concrete quality and the environment. Table 2.3 summarizes some of those equations and shows the factors that have been included (source: Parrott, 1987). It is clear that generally, carbonation depth is dependent on the square root of the exposure period. The other important factors are exposure condition, w/c ratio, strength and chemical composition of cement / concrete.

Factors Influencing Rate of Carbonation

The rate of carbonation of concrete is affected by a number of intrinsic concrete and extrinsic environmental factors. As far as the concrete properties are concerned, the fundamental factor controlling carbonation is the diffusivity of the hardened cement paste, which is a function of the pore system (Neville, 1995). It follows that the factors such as w/c ratio, degree of compaction and hydration (or curing) are all relevant (Richardson, 1988; CEB, 1989; Parrott, 1996). All of these influence the strength of concrete and, therefore, the rate of carbonation is often considered as a function of the strength (Neville, 1995). In general, a reduction in w/c ratio leads to a reduction in carbonation rate due to improved concrete microstructure and reduced porosity, and this has been observed by many researchers (*e.g.* Hamada, 1968; Meyer, 1968; Ho and Lewis; 1983). The effect of curing on carbonation is also substantial, whatever the cement type. Prolonged curing influences

the continuity of voids and by allowing hydration of cement to continue, increases reserve alkalinity (Inoue *et al*, 1970). Dhir *et al* (1989) reported that carbonation depth of specimens cured in water for 1 day, was at least double that of specimens cured for 28 days. Poor compaction tends to increase the carbonation rates due to increased porosity (CEB, 1989).

Table 2.3 Carbonation depth equations (Parrott, 1987)

EQUATION	PARAMETERS
$d = At^n$	d = carbonation depth t = time in years A = diffusion coefficient n = exponent (approximately ½)
$d = ABCt^{0.5}$	A = 1.0 and 1.7 for external and internal exposure, respectively B = 0.07 to 1.0 depending upon surface finish $C = R (w/c - 0.25) / (0.3 (1.15 + 3w/c))^{1/2}$ for w/c ratio ≥ 0.6 $= 0.37R (4.6w/c - 1.7)$ for w/c ratio < 0.6 R = coefficient of neurtalization, a function of mix ingredients
$d = A (Bw/c - C)t^{0.5}$	A is a function of curing B and C are functions of fly ash
$d = 0.43 (w/c - 0.4)(12 (t - 1))^{0.5} + 0.1$	28-day water cured
$d = 0.53 (w/c - 0.2)(12t)^{0.5} + 0.2$	uncured
$d = (2.6 (w/c - 0.3)^2 + 0.16)t^{0.5}$	sheltered
$d = ((w/c - 0.3)^2 + 0.07)t^{0.5}$	unsheltered
$d = 10.3e^{-0.123\ f28}$ at 3 years	unsheltered f_x = x-day compressive strength
$d = 3.4e^{-0.034\ f28}$ at 3 years	sheltered
$d = 680 (f_{28} + 25)^{-1.5} - 0.6$ at 2 years	
$d = A + (B/f_{28}^{0.5}) + (C/(CaO - 46)^{0.5})$ at 1 year	CaO is alkali content expressed as CaO
$d = (0.508/f_{28}^{0.5} - 0.047)(365t)^{0.5}$	
$d = 0.846 (10w/c / (10f_7)^{0.5} - 0.193 - 0.076w/c)(12t)^{0.5} + 0.095$	
$d = A ((t - t_i)\ T^{0.75}\ (C_1/C_2))^{0.5}$	t_i = induction time T = temperature in K $C_1 = CO_2$ concentration $C_2 = CO_2$ bound by concrete

Carbonation is greatly influenced by the relative humidity of the external environment and the resulting moisture condition in the concrete. In very dry conditions, there is likely to be insufficient moisture in the pores for the formation of carbonic acid (Neville, 1995). On the other hand, at very high relative humidity conditions, the diffusion of carbon dioxide is very slow as the moisture presents a barrier to the penetration (Concrete Society, 2000), and is approximately four orders of magnitude lower in water than air (Neville, 1995). The maximum rate of carbonation is observed at an ambient relative humidity of between 50 and 70% (Parrott, 1987).

Other environmental factors that may affect the carbonation process include the concentration of carbon dioxide (Neville, 1995), which may vary locally, and environmental temperature (CEB, 1989). An increase in temperature may increase or decrease the rate of carbonation, depending upon the degree of drying achieved (Concrete Society, 1995).

Carbonation-Induced Corrosion Process

The loss of passivity due to carbonation, *i.e.* the reduction in the pH of the pore fluid from a level in excess of 12.5 to a value as low as 8, leads to anodic and cathodic processes occurring over the bar surface, resulting in corrosion as summarized in the Figure 2.2. There is some uncertainty about the value of pH at which the depassivation occurs. This can occur at a pH of about 11 and does not coincide exactly with the pH value of 9 detected by phenolphthalein indicator, which is often used to test for carbonation (Broomfield, 1997). Saeki *et al* (1984) has reported that corrosion of steel embedded in carbonated mortar when no chlorides were present, initiated at a pH level of about 11.4 and increased rapidly with further pH reductions (cited Parrott, 1987). Therefore, it can be stated that corrosion initiates before the carbonation front reaches the steel and, as the depth of carbonation increases, further reductions in pH increase the corrosion damage (Parrott, 1987; Parrott, 1994).

Carbonation-induced corrosion is normally associated with uniform attack rather than pitting (Glass *et al*, 1991), producing, over the long term, a reduction in the cross sectional area of the steel (Constantinou and Scrivener, 1995; Concrete Society, 2000). Browne (1985) suggests that corrosion layers of thickness less than 0.1 mm can cause damage in the form of cracking and spalling. However, the precise damage occurring is likely to depend on bar size, cover depth, section geometry and concrete grade (Andrade *et al*, 1990).

Factors Influencing Rate of Carbonation-Induced Corrosion

As for the carbonation process, the corrosion rate is influenced by the concrete properties and the environmental factors, but it is evident that once the corrosion is initiated, the rate is mainly controlled by the latter (Tuutti, 1982). The rate of corrosion is only significant where the relative

humidity in the pores adjacent to the steel is higher than about 75%, and rises with an increase in the relative humidity reaching a peak at about 95% and, then, reduces to a very low level near saturation (Tuutti, 1982). According to CEB (1989), the highest risk of corrosion occurs at an effective relative humidity (the relative humidity within the concrete) of between 65 and 85%. The work carried out by Glass *et al* (1991) using carbonated reinforced mortar, reported an exponential increase in corrosion rate as the ambient relative humidity increased above 70% and approached saturation. Therefore, it appears that conditions that promote rapid carbonation are unlikely to result in significant corrosion. While under conditions at which significant corrosion would occur, it is unlikely that the concrete would be carbonated to a significant depth. The low corrosion rates in permanently dry environments (relative humidity less than 60%), in spite of a low pH and a plentiful supply of oxygen, is due to high electrolytic resistance (CEB, 1989). The fact that corrosion increases with an increase in relative humidity (up to about 95%) suggests that the controlling factor is frequently the resistivity of the cover concrete, not the oxygen availability, because oxygen diffusion is restricted at high humidities (Alonso *et al*, 1988; Glass *et al*, 1991; Dhir *et al*, 1992). Corrosion increases with an increase in temperature due to increased rate of chemical reaction and electrolyte conductivity (Glass *et al*, 1991), particularly at temperatures above 20°C, and the effect is slightly more pronounced at higher relative humidities (Raphael and Shalon, 1971 cited Parrott, 1987).

Among other factors that affect the rate of corrosion, the alkalinity of the pore fluids after carbonation, which depends on the cement type, content and degree of hydration (Parrott, 1987). Indeed, Hamada's data (1968) suggest that if other conditions are available for corrosion to occur then, a reduced pH will increase the rate.

Furthermore, Glass *et al* (1991) suggest that concrete with a higher compressive strength and a lower porosity would be expected to have a higher resistivity and support a lower corrosion rate.

However, it has been reported that the normally considered factors governing the corrosion initiation due to carbonation, such as w/c ratio, cement type, concrete cover, degree of curing, exposure conditions during carbonation, are of minor importance for the subsequent corrosion rate (Dhir *et al*, 1992; Parrott, 1994; Constantinou and Scrivener, 1995).

2.3.3 Chloride-Induced Corrosion

Chloride Attack

Chlorides (Cl^-), which destroy the passive oxide layer on embedded steel, can be introduced into concrete via two main routes. They may be present as a result of direct addition to the original concrete mix (use of calcium chloride as an accelerating admixture, sea water as the mix water

and/or contaminated aggregates), and/or dissolved chloride ions may penetrate through the pores to the interior of concrete in structures exposed to coastal environments, de-icing salts and/or other chloride bearing liquids. The use of calcium chloride as an admixture was banned in the amendments made to CP 110 (BSI, 1972) in 1977, and the use of contaminated aggregates and water is strictly limited in BS 882 (BSI, 1992) and BS 3148 (BSI, 1980), respectively. Therefore, it is likely that chlorides from external sources represent the most serious threat in relation to the corrosion of steel in concrete.

Mechanisms of Chloride Transport

Chloride from external sources is transported into the concrete by the medium of water, mainly through diffusion and/or capillary absorption mechanisms (Neville, 1995; Concrete Society, 1996). The diffusion of chloride ions through totally or partially water-filled pores in concrete takes place due to a concentration difference (Kumar *et al*, 1987). This is dominant in submerged or saturated concrete. If a concrete surface is dry or partially dry at the time of contact with a chloride solution then, capillary absorption of the liquid will occur with the accompanying expulsion of air (Chan, 1988). The concrete absorbs the salt water until saturation or until there is no more reservoirs of salt water. Then, further chloride will migrate due to the concentration difference, *i.e.* by diffusion. If, thereafter, concrete undergoes a drying period, this will result in evaporation of pore water and crystallisation of chlorides in the pores. Further wetting will cause further chloride ion transportation into concrete, and those previously deposited will be dissolved and conveyed to a greater depth, creating a concentration gradient. Thus, cyclic wetting and drying cause continuous chloride ingress into concrete through the pores and represent a more critical exposure condition with respect to chloride transportation (Mehta, 1991; Concrete Society, 1996; Hong and Hooton, 1999).

The chloride penetration through concrete is based on a combination of mechanisms rather than pure diffusion, depending on the local prevailing exposure conditions, the pore saturation and the concrete microstructure (Dhir *et al*, 1998; De Schutter, 1999; Hillier *et al*, 2000). However, it can be best represented by a diffusion process if the concrete is assumed to be relatively moist (Stewart and Rosowsky, 1997). In this case, the chloride penetration is given by Fick's laws of diffusion, assuming that the substrate is homogeneous, isotropic and inert. The assumptions, therefore, imply that the diffusion properties at any point in concrete would be the same in all directions and do not change with time (Dhir *et al*, 1998).

According to Fick's first law, the rate of transfer of a diffusant through a unit area perpendicular to the direction of diffusion is proportional to the concentration gradient (Crank, 1975). The negative sign arises as the diffusion occurs in the opposite direction to that of increasing concentration.

$$J = - D (dC/dx)$$

where J = flux (mole/cm^2.s)

D = coefficient of chloride diffusion (cm^2/s)

dC/dx = concentration gradient (mole/cm^3.cm)

In Fick's second law, the flux is eliminated by employing the concept of the mass conservation (Daniels and Alberty, 1975).

$$(dC/dt) = D (d^2C/dx^2)$$

where C = chloride ion concentration (g/cm^3)

t = time (s)

D = coefficient of chloride diffusion (cm^2/s)

x = distance (cm)

In reality, concrete is inhomogeneous, anisotropic and reactive. In addition, due to continuing hydration and other ageing effects such as micro-cracking and autogenous healing, the concrete composition as well as its microstructure will vary with both the exposure time and the distance from the concrete surface (Dhir *et al*, 1998). Therefore, in the long-term, prediction of chloride diffusion on the basis of above laws may not be accurate (Buenfeld and Newman, 1987; Mangat and Molloy, 1994a; Dhir *et al*, 1998; Costa and Appleton, 1999).

Nature of Chlorides in Concrete

There are other mechanisms including chloride binding that influence the progress and rate of chloride ingress (Broomfield, 1997). Chlorides can be physically adsorbed to the surface of the gel pores or chemically bound within the hydrated compounds in concrete (Neville, 1995). Thus, chloride ions present in hardened concrete may exist in one or more of the three forms, free, physically adsorbed and chemically bound (Berman, 1972; Neville, 1995). However, the distribution of the chloride ions between these three forms is neither permanent nor clear (Glass and Buenfeld, 1997), and there is always an equilibrium situation such that some free chlorides are present in the pore water (CEB, 1989). Neville (1995) argues that only chloride ions, in excess of those needed for this equilibrium, can become bound. Therefore, when more and more chloride ions penetrate into concrete, it is likely to increase the chloride ions required for the equilibrium and binding mechanisms, mentioned above (both free and bound chlorides are likely to be increased).

In the literature, chloride content is expressed in terms of total (bound and free) or water-soluble, also sometimes referred to as free chlorides. In addition, the acid-soluble chloride content, often mistakenly called total chloride content, is also used (ACI Committee 222R, 1996). Gaynor (1987)

suggests that approximately 50 to 75% of acid-soluble chlorides are soluble in water. Neville (1995) mentions that free chloride content can vary from about 50% to as low as 20% of the total chloride content. It is generally recognised that corrosion is influenced by the free chloride ions in the pore solution and not the total chlorides (CEB, 1989; Concrete Society, 1995; Neville, 1995). However, recent work of Glass and Buenfeld (1997) and Glass *et al* (2000), suggest that bound chloride presents a corrosion risk.

Factors Influencing Rate of Chloride Penetration

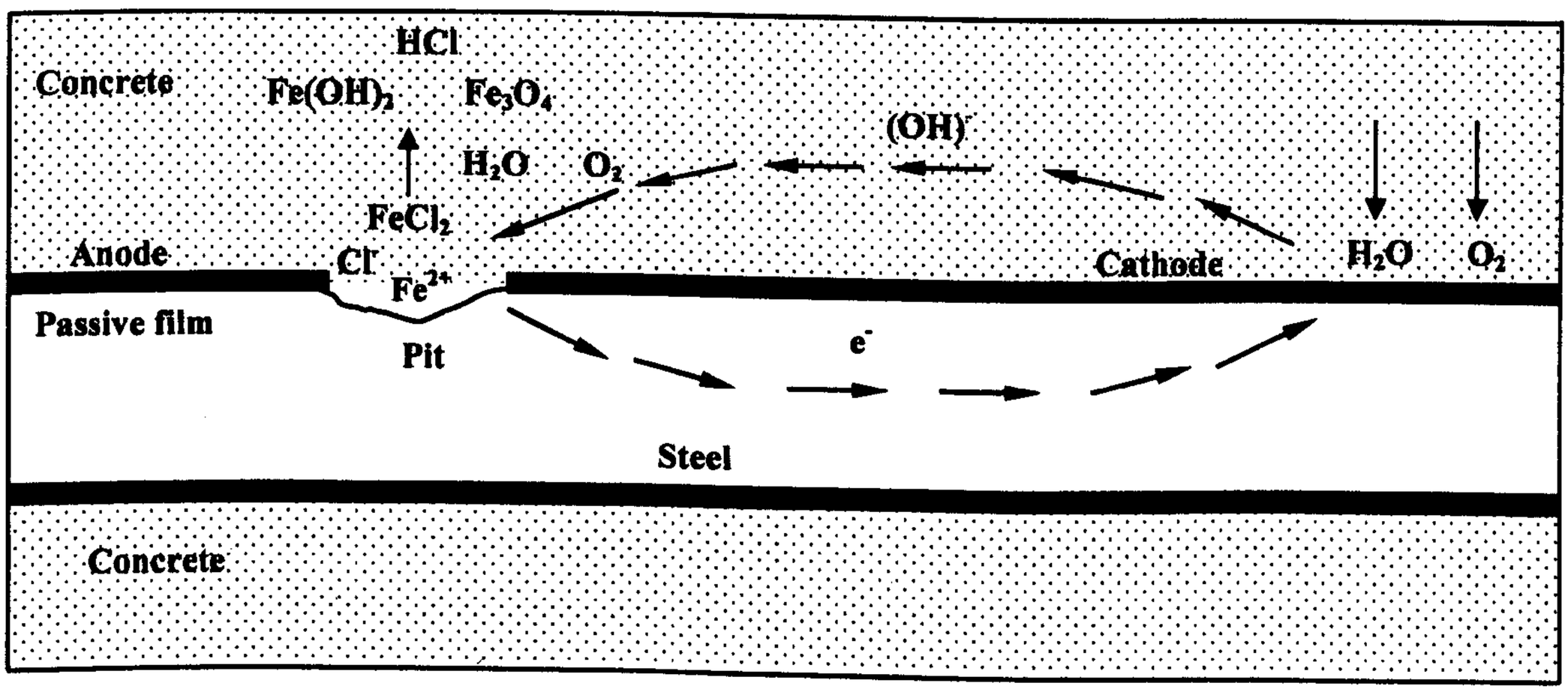
The penetration of chlorides into hardened concrete is influenced by many parameters related to both the concrete properties and the environmental characteristics. The w/c ratio directly affects the number, size and continuity of pores in hydrated cement paste. Therefore, generally, with an increase in w/c ratio, more pores and flow paths are formed decreasing the resistance to chloride ingress for a given degree of hydration. This has been observed by many researchers (Page *et al*, 1981; Jaegermann, 1990; Leng *et al*, 2000). The curing, which is significant with respect to the development of the concrete microstructure, also influences the passage of chloride ions (Mehta, 1991; Neville, 1995; Bentur *et al*, 1997). Dhir *et al* (1995) observed that the resistance to chloride penetration, hence the time to corrosion initiation, was reduced by approximately 70% when concrete specimens were air-cured at 20°C and 55% relative humidity, instead of water-curing at 20°C to 28 days. The same authors suggest that if other conditions are not changed, the resistance to chloride penetration increases with concrete grade. In addition, poor compaction increases the degree of chloride penetration into the concrete due to increased porosity (CEB, 1989). Generally, concrete with improved microstructure and higher chloride binding capacity has better resistance to chloride penetration. Therefore, cement composition and cement type, which affect chloride binding, concrete microstructure and pore fluid chemistry, can influence the chloride ingress into the concrete (CEB, 1989; Neville, 1995; Concrete Society, 1996; Bentur *et al*, 1997; Leng *et al*, 2000).

As mentioned earlier, chloride penetration through concrete is most rapid under cyclic wetting and drying exposure conditions. Thus, environmental factors such as temperature, rainfall and relative humidity, which govern the degree and frequency of wetting and drying, are important with respect to chloride penetration (Concrete Society, 1996; Hong and Hooton, 1999). In addition, as the diffusion process is thermally activated, chloride ingress through concrete is expected to increase with temperature at saturated conditions (Bentur *et al*, 1997). While the influence of the external chloride concentration on the chloride penetration through concrete has not been widely investigated, Andrade *et al* (1996) suggest that the chloride diffusion coefficient decreases with the increasing external chloride concentration. This is due to reduced ionic mobility at higher ion concentrations causing an increasing number of ion-ion interactions.

Chloride-Induced Corrosion Process

In the presence of significant quantities of chloride ions at the level of the reinforcing steel, the protective passive layer is broken down. However, the precise nature of depassivation due to chloride ions is still a subject for debate (Treadaway, 1988; ACI Committee 222R, 1996). The chloride ions attack the passive layer but, unlike carbonation, there is no overall drop in pH prior to depassivation (Broomfield, 1997; Concrete Society, 2000). Thereafter, in the presence of oxygen and moisture, corrosion, in the form of pits, can occur and the process is sustained when chloride ions are further drawn to the steel by positively charged ferrous ions at the anode (Mehta, 1991). Other factors associated with concrete that influence pit formation include good electrical conductivity and a high alkali content (Arup, 1983).

A schematic illustration (Treadaway, 1988) of the corrosion process and the chemical reactions involved are given in Figure 2.4. Thus, chloride ions are regenerated so that rust contains no chlorides, although ferrous chloride is formed at an intermediate stage. In other words, chloride ions are not consumed in the corrosion process, but help to break down the passive layer. In addition, as the pitting process occurs, it leads to hydrochloric acid formation in the pits.



Anodic Reactions

$Fe \rightarrow Fe^{2+} + 2e^-$

$Fe^{2+} + 2Cl^- \rightarrow FeCl_2$ (ferrous chloride)

In the presence of water: $FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$ (hydrochloric acid)

In the presence of oxygen and water: $6FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12HCl$

Cathodic Reaction

$4e^- + O_2 + 2H_2O \rightarrow 4(OH)^-$

Figure 2.4 Schematic representation and chemical reactions involved in pitting corrosion (Treadaway, 1988)

The precise mechanism of pit formation remains to be completely resolved (Treadaway, 1988) and several intermediate and final products can be formed during steel corrosion (Mehta, 1991). The nature of pitting is such that at conditions of low pH, the corrosion products may be dissolved. Therefore, it is possible that significant pitting may occur prior to any visible appearance on the concrete surface (Concrete Society, 1995). This process is normally characterised by highly localised corrosion (anodic areas, pits) when sufficient oxygen and water are available, separated by large cathodic areas (Page, 1988; Treadaway, 1988; Broomfield, 1997). This is known as macro-cell phenomenon.

Critical Threshold Chloride Levels

The chloride concentration at the surrounding of the steel bars must reach a critical threshold value to result in a breakdown of the passive film, thereby initiating corrosion. This depends on several factors such as concrete mix proportions, cement type and composition, w/c ratio, alkalinity of the pore fluid, temperature, relative humidity, water and oxygen availability, steel surface conditions and source of chloride (Stewart and Rosowsky, 1997; Alonso *et al*, 2000). Given the range of factors, there is a lack of agreement on the chloride threshold value itself and its definition, both in terms of its determination (visual observation, corrosion potential or corrosion current) and means of expression (water-soluble, acid-soluble or total chloride as chloride / hydroxyl ion concentration (Cl^-/OH^-) ratio, percentage of the weight of cement or concrete). Thus, it is to be expected that the critical threshold chloride concentration will vary even for similar structures (Stewart and Rosowsky, 1997), and the adoption of a single value for the purpose of specification or service life prediction is inappropriate (Thomas, 1996). Various studies have reported a range of critical thresholds, as given in Table 2.4.

A review carried out by Glass and Buenfeld (1997) suggests that chloride threshold values should be presented as total chloride contents expressed relative to the weight of cement. This may be viewed as the total potential aggressive ion content expressed relative to the total potential inhibitor content. Furthermore, to justify this, as mentioned earlier, it is considered that bound chlorides present some corrosion risk, opposing the generally accepted view that only free chlorides cause corrosion. The data of several authors, taken from field and laboratory studies in mortar and concrete, indicate that total chloride thresholds may vary by more than one order of magnitude (from 0.097 to 3.04% by weight of cement), as pointed out by Alonso *et al* (2000). The same authors notice a higher range for water-soluble chloride thresholds from 0.14 to 1.15% by weight of cement. However, early work argued that the chloride threshold level is best expressed as the Cl^-/OH^- ratio (Hausmann, 1967; Gouda, 1970) and suggested a critical Cl^-/OH^- ratio of around 0.6 in simulated concrete pore solutions. This is not readily measured, but approximates to a

concentration of 0.4% chloride by weight of cement if chlorides are cast into concrete and 0.2% if they diffuse in (Broomfield, 1997).

Table 2.4 Critical threshold chloride levels proposed from previous studies

REFERENCE	DEPASSIVATION DETECTION METHOD	% CHLORIDES BY WEIGHT OF CEMENT
Total Chlorides		
Gouda and Halaka (1970)	Anodic polarization	1.01 – 3.04
Hope and Ip (1987)	Corrosion rate, AC impedance, visual inspection and gravimetric mass loss	0.097 – 0.190
Hansson and Sorensen (1988)	Corrosion current density	0.6 –1.4
Thomas *et al* (1990)	Visual observation and mass loss	0.5
Pettersson (1996)	Corrosion rate	0.5 – 1.8
Schiessl and Breit (1996)	Macro-cell current	0.5 - 1.5
Thomas (1996)	Mass loss	0.2 – 0.7
Alonso *et al* (2000)	Corrosion current density	1.24 – 3.08
Water-Soluble Chlorides		
McCarthy (1991)	Corrosion current density	0.25 – 0.65
Dhir *et al* (1995)	Corrosion current density	0.34 – 0.62
Alonso *et al* (2000)	Corrosion current density	0.39 – 1.16

Two maximum allowable limits are given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002) for the total chloride content in reinforced concrete, *i.e.* 0.2 and 0.4% by the mass of cement, depending on the cement type. It should be noted that in these standards, the total chloride means the sum of the individual chloride contents of the constituent materials used in mix proportions. The approach of the ACI Committee 318/318R (ACI, 1999) is to consider limits on the water-soluble chlorides in concrete, contributed by the mix ingredients, and the maximum chloride ion content of reinforced concrete at ages from 28 to 42 days is limited to 0.15% by the mass of cement. ACI Committee 222R (ACI, 1996) suggests a more conservative approach limiting the acid-soluble and water-soluble chloride contents (by the mass of Portland cement) in reinforced concrete to 0.1 - 0.2% and 0.08 - 0.15%, respectively, depending on the moisture conditions.

In spite of the uncertainty of the chloride threshold value, to provide a guide to engineers, Everett and Treadaway (1980) have proposed the following classification for corrosion risk, based on the total chloride content when expressed as a percentage of the weight of cement.

Low risk	<	0.4%
Medium risk		0.4 to 1.0%
High risk	>	1.0%

This corrosion risk classification, which provides some practical guidance, is generally in good agreement with the guidelines published by Brown (1982) using the total chloride content by the mass of cement, as sown below.

Negligible risk	<	0.4%
Possible risk		0.4 to 1.0%
Probable risk		1.0 to 2.0%
Significant risk	>	2.0%

Factors Influencing Rate of Chloride-Induced Corrosion

Once corrosion starts, the rate at which damage occurs and its overall severity are influenced by a complex interaction of factors relating to both the concrete characteristics and the environment (Arup, 1983; Page *et al*, 1986; Treadaway, 1988). However, the individual contribution of these factors to the overall rate of corrosion is difficult to determine, especially in field practice (Dhir *et al*, 1995). As mentioned earlier, the availability of oxygen at the steel surface and the electrical resistivity of the concrete, which is a function of its moisture condition, cement content and type, are the controlling factors of corrosion rate, once initiated (Mehta, 1991; Neville, 1995). It should be noted that the concrete microstructure, pore fluid content and chemistry, which influence the transport of chlorides, also control the availability of oxygen and moisture (Neville, 1995). Thus, the corrosion rate is affected by factors including w/c ratio, curing and degree of compaction. As the w/c ratio of concrete reduces, the corrosion rate decreases significantly (Mehta, 1991; Hawkins and McKenzie, 1996). Similarly, Dhir *et al* (1995) report data that show that the rate of corrosion reduces with concrete strength. The rate of corrosion is significantly higher in the air-cured concrete compared to that of water-cured concrete, once initiated (Dhir *et al*, 1995). The thickness of the concrete cover also affects the oxygen availability (Mehta, 1991) and the moisture condition (Hawkins and McKenzie, 1996) at the steel surface and, therefore, increased cover results in reduced corrosion rates. Hawkins and McKenzie (1996) suggest that the effect of the concrete cover with respect to corrosion rate is more sensitive under high humidity conditions. In addition, the resistivity of the concrete is reduced if different cement types are used effectively due to denser microstructure and modified pore chemistry, and this causes reduced corrosion rates (Hope and Lp, 1987; Rasheeduzzafar *et al*, 1987; Hussain and Rasheeduzzafar, 1994).

It should be noted that the oxygen flux is greatly controlled by the moisture condition of concrete (Lawrence, 1990). As the moisture content in concrete increases, oxygen diffusivity drops to very low values, being at a minimum in fully saturated concrete. This is beneficial from the standpoint of corrosion, on the other hand, it sharply reduces the electrical resistivity of concrete, which controls the corrosion rate (Mehta, 1991). When the moisture content of concrete decreases, both the availability of oxygen at the steel surface and the electrical resistivity of the concrete are increased and, it is, therefore, not surprising that the maximum corrosion rate occurs under alternate wetting and drying conditions. Thus, the conditions that are critical for chloride penetration support higher corrosion rates as well. According to CEB (1989), there is a high risk of corrosion in chloride contaminated concrete when the relative humidity within concrete is in the region of 65 to 98%. It is worth mentioning that chloride-induced corrosion can occur at low ambient relative humidity conditions (50 to 60%) due to the hygroscopic effect of chloride ions (CEB, 1989), but the rate will not be high.

The chemical reactions associated with corrosion occur at a faster rate at higher temperatures, reflecting the possible decomposition of the bound chlorides under these conditions (Neville, 1995). Indeed, an increase in temperature leads to higher corrosion rates, as observed by Hawkins and McKenzie (1996) and Maslehuddin *et al* (1996).

In addition, it appears that there is some disagreement regarding the influence of chloride ion concentration on the corrosion rate, once initiated. Al-Amoudi *et al* (1991) found that above a critical threshold value, the corrosion rate is similar for all chloride concentrations, whereas other researchers suggest that the corrosion rate increases with chloride ion concentration (Arya and Xu, 1995; Dhir *et al*, 1995).

2.3.4 Corrosion in Cracked Concrete

When the tensile strain to which concrete is subjected, exceeds the tensile strain capacity of concrete, intrinsic and extrinsic cracks will occur. In concrete structures, tensile stresses may originate mainly due to the restraint against volumetric change (from physical, chemical, thermal causes) and/or loading (from structural causes). These cracks can be categorised as coincident cracks following the line of reinforcement or intersecting cracks crossing the reinforcement (Concrete Society, 1995). It is probable that cracks permit greater migration of moisture, oxygen and aggressive agents through the concrete, making the steel more susceptible to corrosion (ACI Committee 224R, 1990; Stewart and Rosowsky, 1997). A schematic description of the advance of a depassivating agent (carbonation front or critical chloride ion profile) in a region of a crack is given in Figure 2.5 (suggested by Beeby, 1979). Several studies have shown that increases in the rate at which the carbonation front (Schiessel, 1975; De Schutter, 1999) and chloride ion

(De Schutter, 1999; Francois and Arliguie, 1999; Li, 2001) penetrate occur with increasing crack width. In addition, De Schutter (1999) suggests that the influence of cracks on the chloride penetration is significantly higher than on the carbonation.

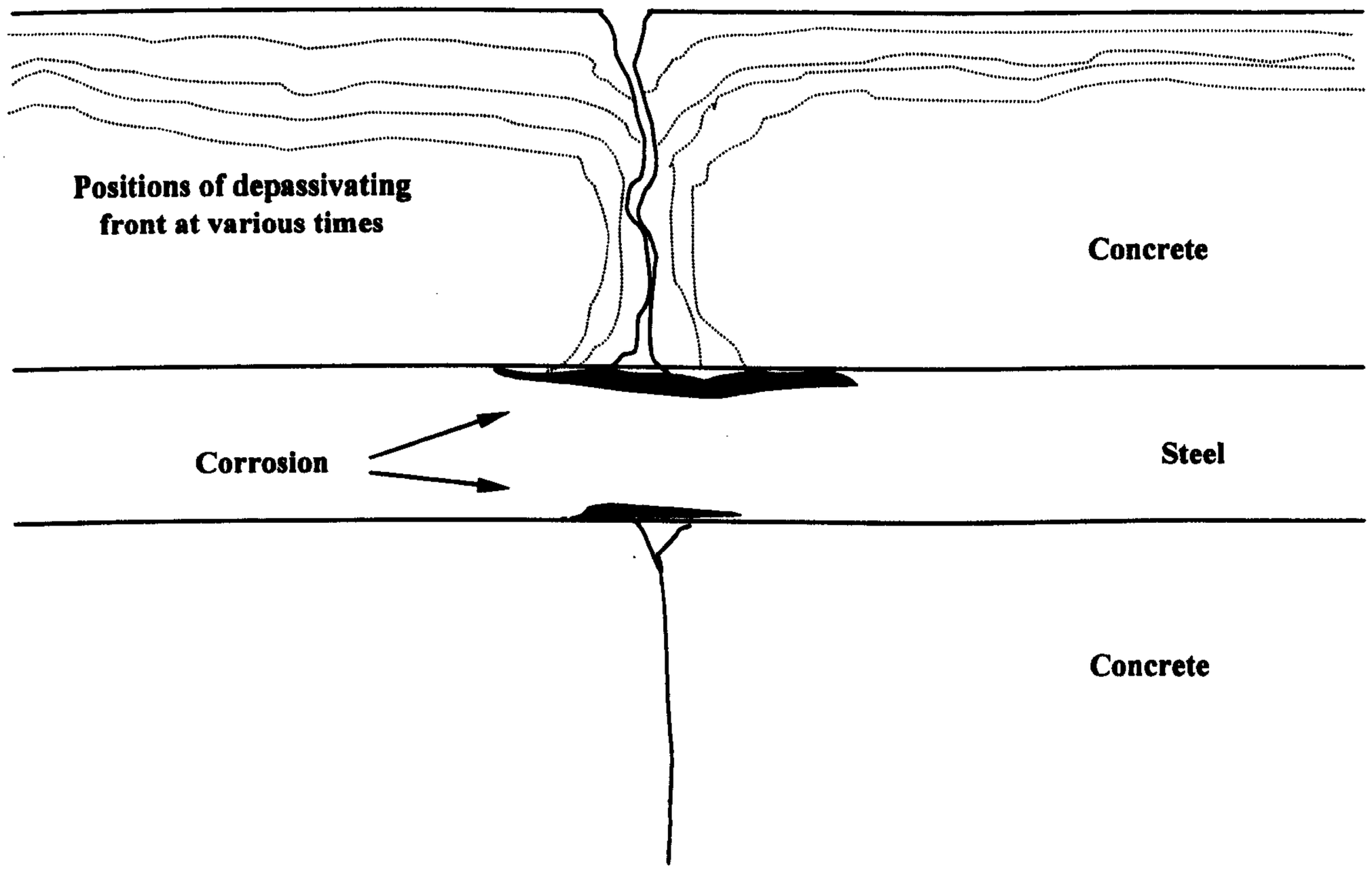


Figure 2.5 Schematic description of the advance of a depassivating agent in a region of a crack (Beeby, 1979)

Corrosion normally starts first where a bar meets a crack and, in the short term, there is a significant influence of the crack width on the amount of corrosion found near a crack (Beeby, 1978; Ohno *et al*, 1996). In other words, the corrosion initiation is accelerated by the crack width. Li (2001) suggests that once the crack width is greater than 0.1 mm, the cracking has a considerable impact on chloride induced corrosion initiation. In contrast, it has been shown that corrosion initiation is not significantly affected by surface crack widths less than 0.3 to 0.6 mm (Gergely, 1981; Wilkins and Lawrence, 1983). As far as the rate of corrosion propagation is concerned, coincident cracks will break down the passivity of steel at many locations and accelerate the rate of corrosion as long as oxygen and moisture are readily transmitted to the cathodic areas through cracks (ACI Committee 224.1R, 1993; Concrete Society, 1995). On the other hand, the influence of crack width of intersecting cracks on the rate of corrosion is negligible (Beeby, 1978; ACI Committee 224.1R, 1993; Concrete Society, 1995). This is because the exposed portion of a bar at an intersecting crack normally acts as an anode and the passive steel forms the cathode; the rate of corrosion is controlled by the availability of oxygen and moisture, not at the

crack, but in the sound concrete, and the electrical resistivity between the anode and the cathode. Thus, the rate of corrosion is limited by the same factors as for the uncracked concrete (Beeby, 1978; ACI Committee 224.1R, 1993; Concrete Society, 1995; Bentur *et al*, 1997).

It is, therefore, difficult to introduce a critical threshold crack width for the rate of corrosion propagation, which depends on crack orientation (Beeby, 1978). Instead, the rate of corrosion propagation is influenced by many factors, such as crack properties, concrete and steel properties and service environment (Concrete Society; 1995). Based on long-term experimental work, Francois and Arliguie (1999) conclude that the degree of chloride-induced corrosion is not influenced by the intersecting crack width (up to 0.5 mm). According to CEB (1989) and Broomfield (1997), the influence of intersecting cracks up to about 0.4 to 0.5 mm on the corrosion rate is relatively small and any on-going corrosion is likely to come to a halt due to self-healing effects. The maximum allowable crack width specified in BS 8110: Part 2 (BSI, 1985) for reinforced concrete structures in aggressive environments is 0.3 mm, but the limit given in ACI Committee 224R (1990) varies from 0.1 to 0.4 mm, depending on the nature of the aggressive environment expected.

It must be noted that most research work have been done using reinforced concrete where the cracks are intersecting. They indicate that the quality of the concrete and the cover have a much greater influence than the intersecting crack width on the corrosion as it is governed by the same factors as for uncracked concrete. The principal factor affecting chloride-induced corrosion in cracked (intersecting) concrete appears to be w/c ratio and the degree of corrosion increases as the w/c ratio is increased (Ohno *et al*, 1996; Schiessel and Raupach, 1997; Li, 2000 and 2001). Schiessel and Raupach (1997) suggesting that increased concrete cover reduces the chloride-induced corrosion rate significantly. The experimental results of Li (2000 and 2001) indicate, perhaps, as might be expected that there is a negligible effect of cement type on the chloride-induced corrosion initiation in cracked (intersecting) concrete specimens.

2.4 INFLUENCE OF CEMENT CONTENT ON CONCRETE PROPERTIES

Given the lack of agreement in specifications to minimum cement content requirements (see Section 2.2), this section reviews the published literature on the influence of cement content at fixed w/c ratio on concrete properties. This includes fresh, engineering, permeation and durability properties and resistance of concrete to reinforcement corrosion.

It should be noted that the majority of studies in this review did not directly address the issue of role of cement content on concrete performance. Instead, some investigated the influence of aggregate / cement (a/c) ratio on concrete properties while others examined new test techniques and

tested a wide range of mixes to establish their suitability. In addition, some studies investigated the effect of using water-reducing or superplasticizing admixtures to allow water contents to be reduced.

In some studies, mix proportions were not given but were derived from other data provided (*e.g.* a/c ratio, particle density, *etc.*). In addition, test specimens and procedures were varied between studies and these detailed information are given in Appendix A. Unless noted otherwise, the results discussed for hardened concrete properties are for specimens made with Portland cement.

2.4.1 Fresh Properties

Workability

The workability of fixed w/c ratio concrete and mortar mixes has been varied with cement content between zero and collapse slump (Collins, 1950; Erntroy and Shacklock, 1955; Keene, 1960; Welch, 1961; Hobbs, 1972; Dhir *et al*, 1987b; Dhir *et al*, 1989b; Loo *et al*, 1994). In general, least workability was measured at lowest cement content due to corresponding reduction in the water content of the mix. It is to be noted that some of the low workability mixes would have been unpractical for placement in reinforced concrete sections. Therefore, in a few studies (Dhir *et al*, 1987a; Mills, 1987; Tanahashi *et al*, 1987; Dhir *et al*, 1996; McCarthy *et al*, 1996), water-reducing or superplasticizing admixtures were used in mixes having reduced cement and water contents to maintain workability and were found to perform satisfactorily.

Other Properties

There appears to be very little published data on cohesion, finishability, bleeding, air content and heat of hydration characteristics of concrete. Tham (1984) has reported that the performance of concrete in terms of both bleeding and temperature rise was improved as the cement content reduced at fixed w/c ratio. Significant reductions in bleeding in cement-and-water-reduced mixes were attributed to the lower water content. Lower maximum temperatures in cement-and-water-reduced mixes were due to the reduced cement content as the cement content itself controls the temperature rise due to the exothermic nature of hydration reactions. The author suggested that a reduction in temperature rise was significant at low w/c ratio.

2.4.2 Engineering Properties

Compressive Strength

The influence of variation in cement content on strength has been examined mainly at fixed free w/c ratio. However, in some early studies (pre-1960), comparisons were made at fixed total w/c ratio since no allowance was made for absorption of mix water by the aggregate.

Mixes having fixed free water / cement ratios

Figure 2.6 shows compressive strength results (100 mm cube) plotted against cement content for concrete mixes having a range of fixed free w/c ratios and containing PC, natural gravel and sand. In this (and all other figures), water contents of mixes are indicated beside the data points and w/c ratios are given near data series. In general, at fixed free w/c ratio, cement and water reduction is not detrimental to concrete strength and may increase it slightly. This behaviour was observed over a wide range of w/c ratios (from 0.76 to 0.35). Essentially, similar behaviour was observed for PC mixes made with aggregates other than natural gravel and sand (see Figure 2.7) and for concrete mixes made with different cement types (PC, PC / PFA and PC / GGBS), see Figure 2.8. In addition, several authors have reported that nominal strength grade was maintained with variation in cement and water contents at fixed free w/c ratio, both with (Dhir *et al*, 1996; McCarthy *et al*, 1996) and without (Dhir *et al*, 1987b; Dhir *et al*, 1989b; Dhir *et al*, 1991; Loo et al, 1994) inclusion of a chemical admixture to maintain workability. Furthermore, it appears that curing regime (water or air) does not influence the behaviour (Hughes and Ash, 1968; Dhir *et al*, 1987b).

Little discussion is given in the literature to the mechanisms of strength gain with cement reduction at fixed w/c ratio. However, there are likely to be several contributing factors including increased aggregate and reduced cement paste contents and fewer voids in the hardened concrete due to the reduced water content. In addition, with reduced water and increased aggregate contents, less damage is likely to occur to the paste / aggregate particle bond due to reduced bleeding and drying shrinkage. For cement-reduced mixes containing water-reducing or superplasticizing admixtures, potential for greater hydration of PC through dispersion of flocs by the chemical admixture may be a contributing factor to the observed behaviour. However, this effect appears to be relatively minor, given that the strength changes occurring with variation in cement and water contents were essentially similar between concrete mixes made with-and-without admixtures.

Mixes having fixed total water / cement ratios

In many early studies, no allowance was made in the mix proportions for water absorption by the aggregates, *i.e.* the quantity of water available for hydration (free water) was lower than that added to the mixer (total water). Figure 2.9 shows strength results plotted against cement content for mixes having fixed total w/c ratio and, in the main, made with PC, natural gravel and sand. In general, there was a tendency for slightly higher strength at lowest cement (and water) content, although Keene (1960) observed no significant effect of variation in cement content on the strength. The changes occurring were essentially similar between normal (Wright and McCubbin, 1952; Singh, 1958) and high (Collins, 1950; Erntroy and Shacklock, 1955) strength concrete. In addition to the mechanisms discussed earlier, the observed behaviour partly reflects greater

absorption of water by aggregates in leaner mixes (mixes with lower cement content) owing to increased aggregate content and consequent reduction in free w/c ratio.

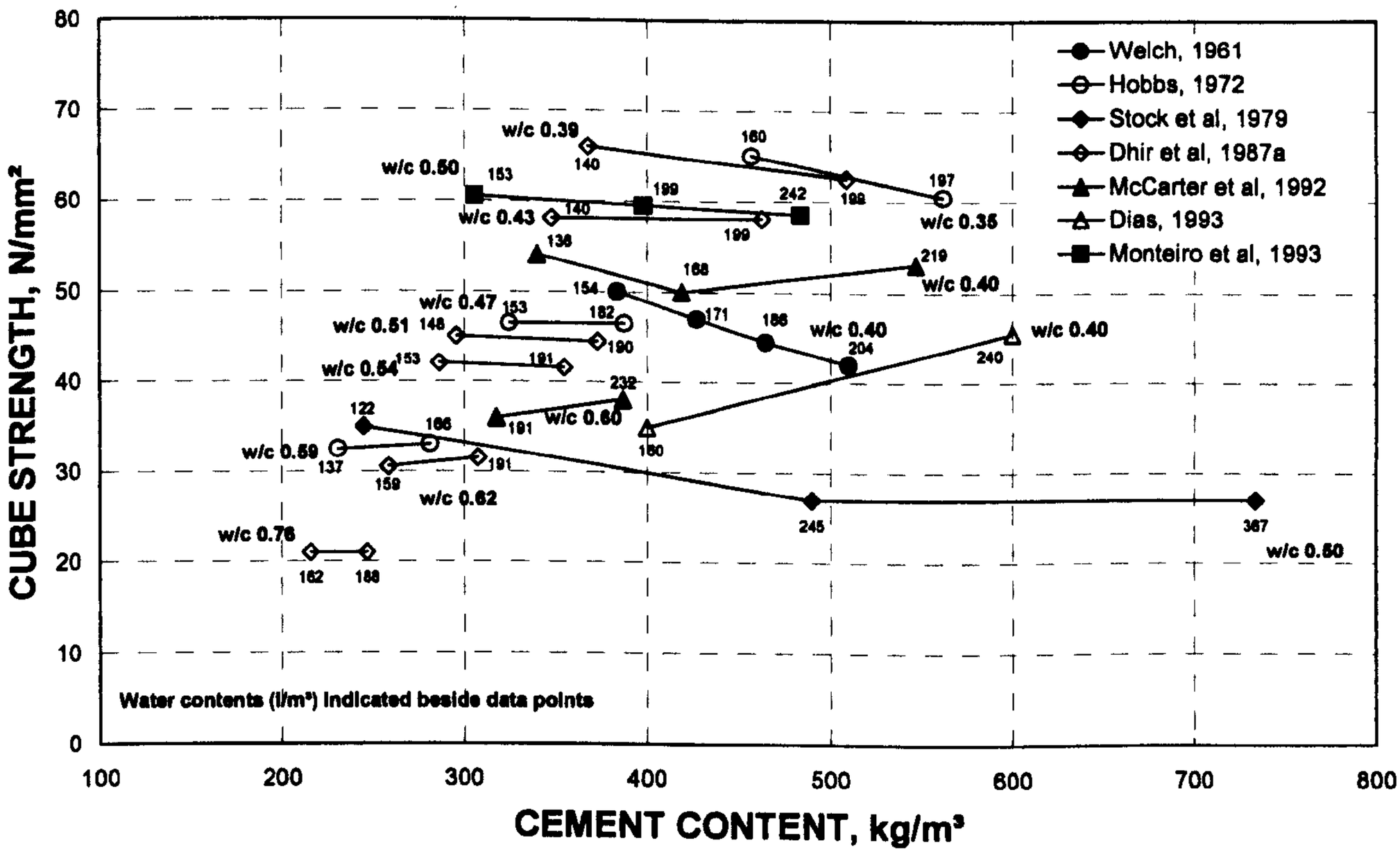


Figure 2.6 Influence on compressive strength of variation in cement and water contents at fixed free w/c ratio for concrete made with PC and natural gravel

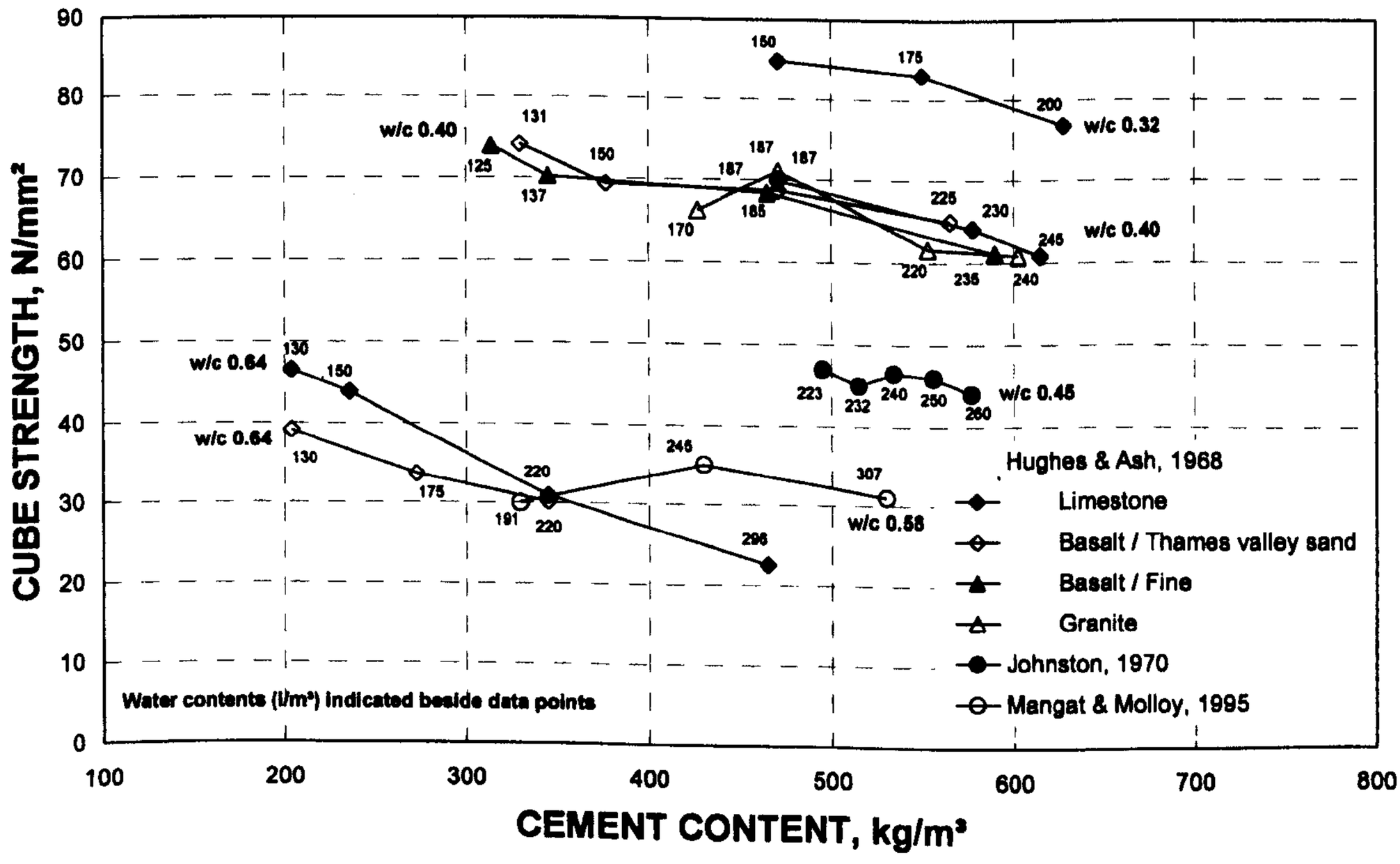


Figure 2.7 Influence on compressive strength of variation in cement and water contents at fixed free w/c ratio for concrete made with PC and other coarse aggregates

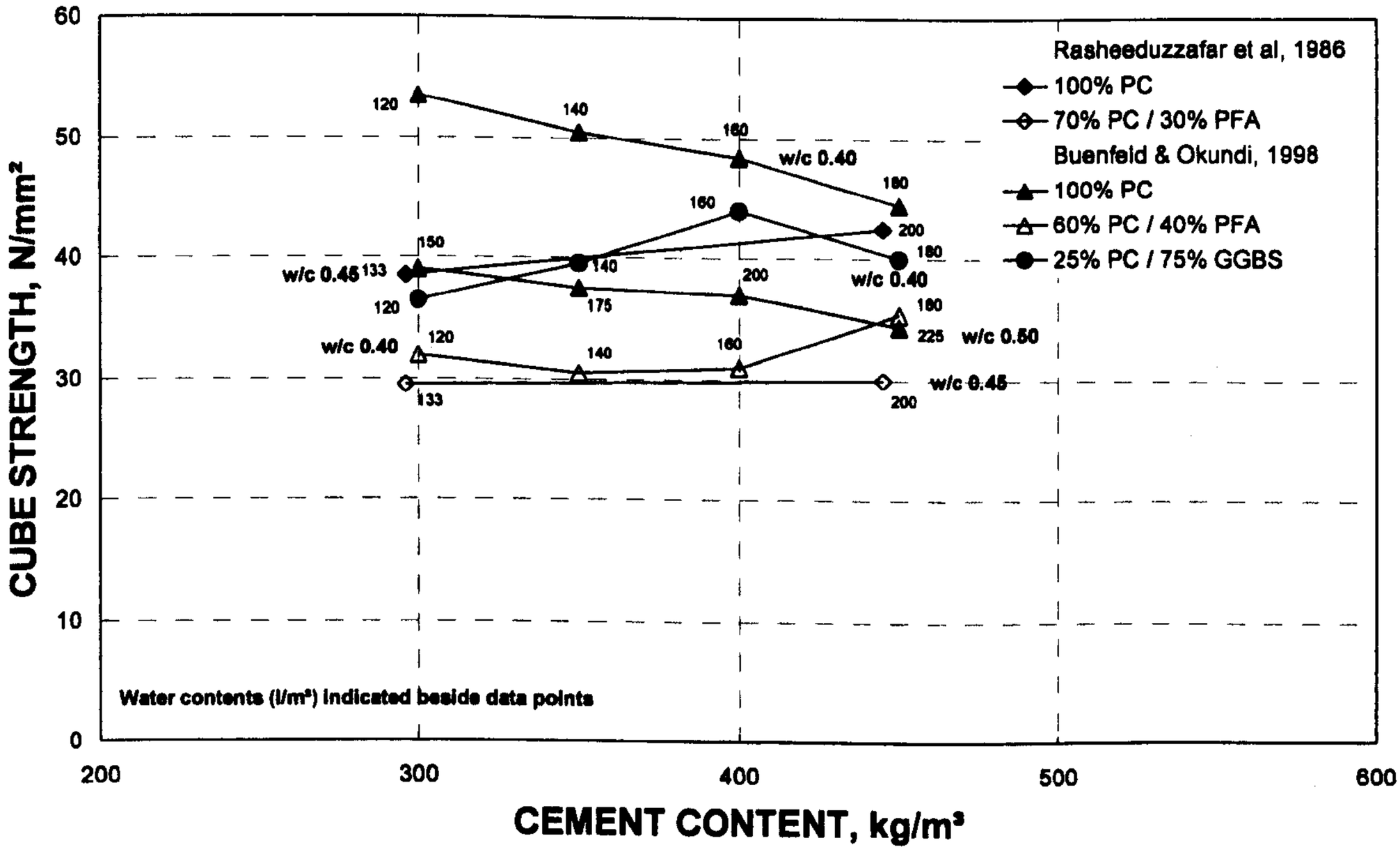


Figure 2.8 Influence on compressive strength of variation in cement and water contents at fixed free w/c ratio for concrete made with different cements

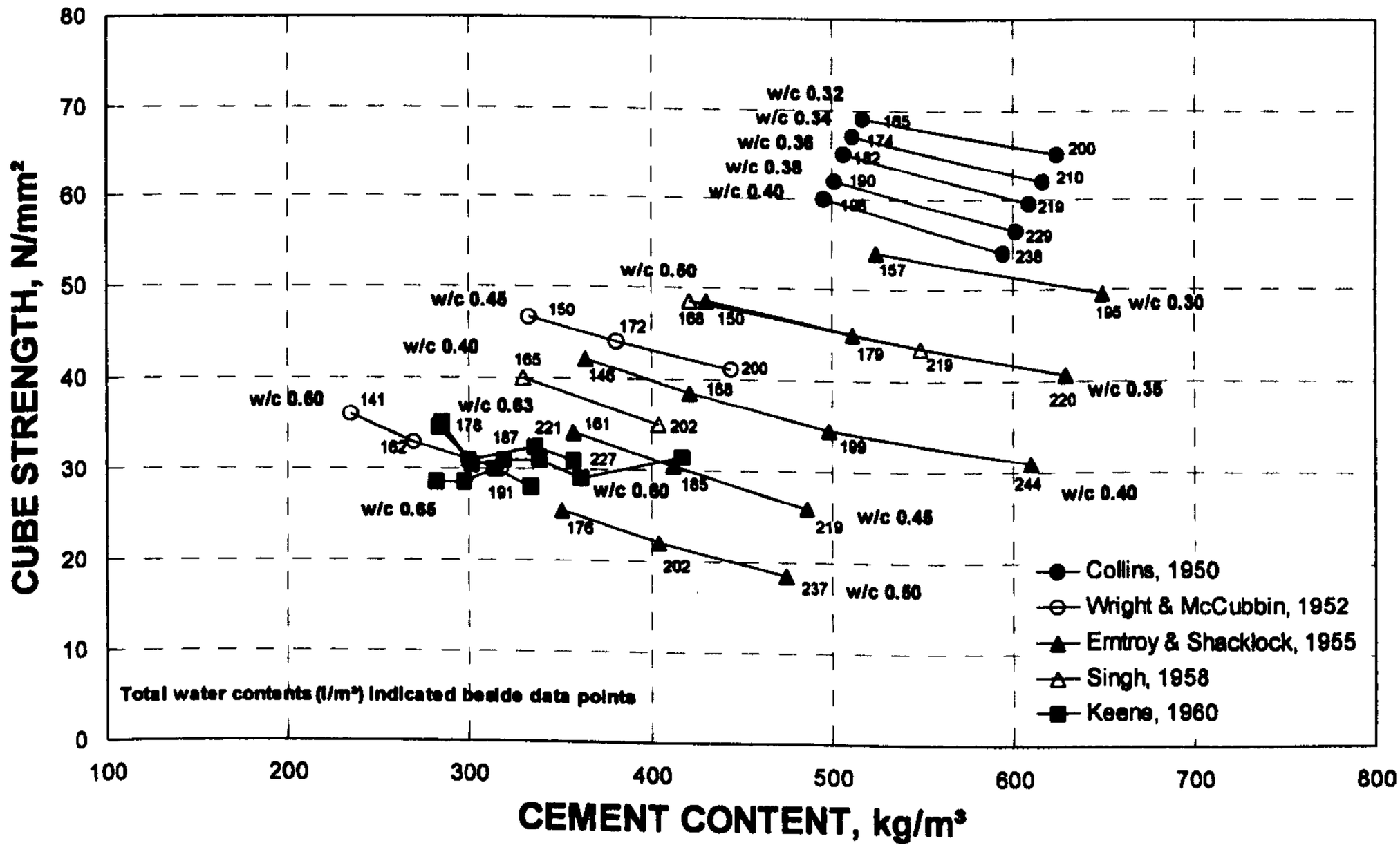


Figure 2.9 Influence on compressive strength of variation in cement and water contents at fixed total w/c ratio for concrete made with PC and natural gravel

Collins (1950) also tested mixes containing other aggregate combinations, see Figure 2.10. The results indicated a greater rate of strength gain with cement reduction for mixes made with various crushed aggregates (typically 6.0 N/mm² per 100 kg/m³ cement reduction), compared to those made with natural gravel and sand (typically 4.0 N/mm² per 100 kg/m³ cement reduction).

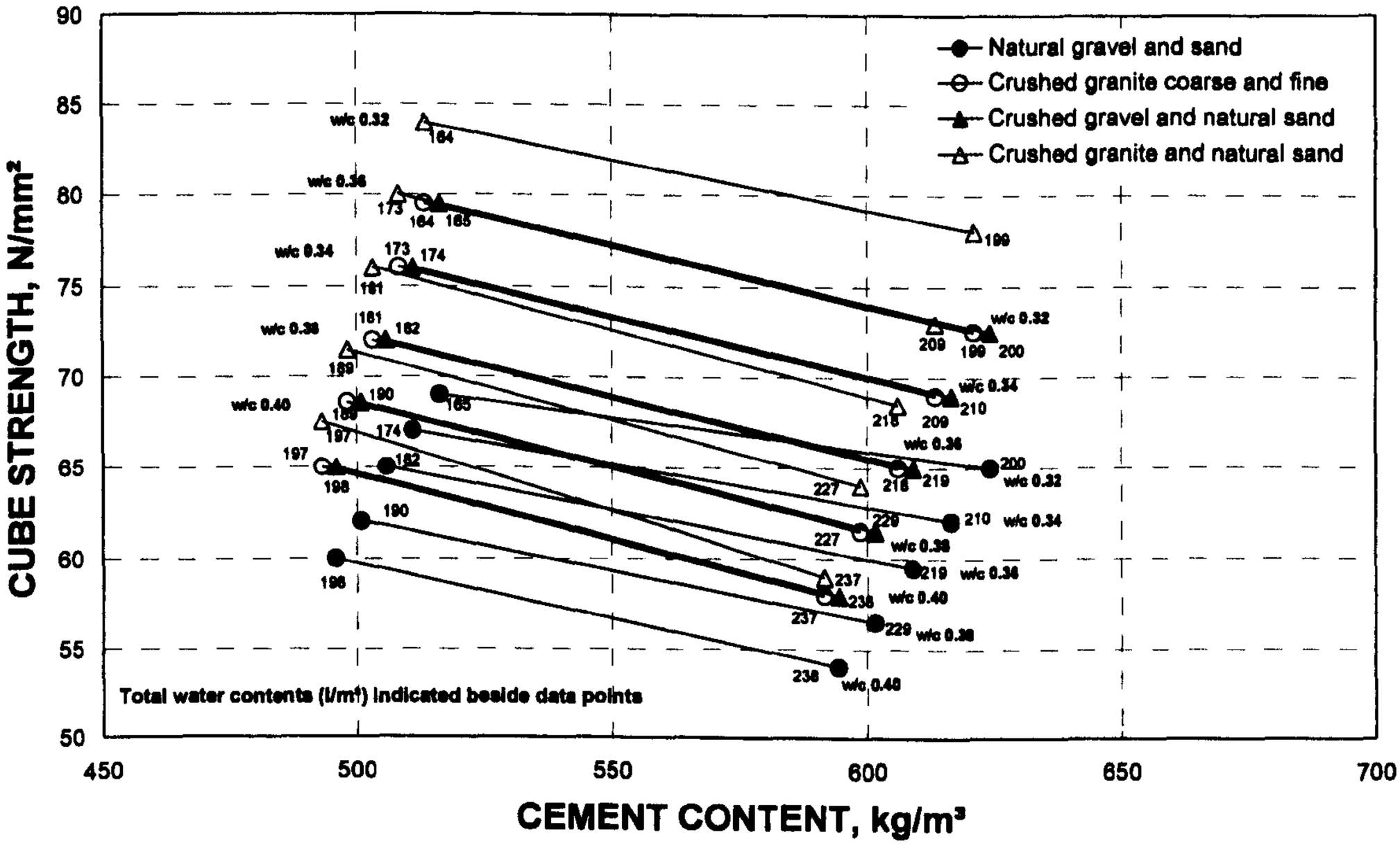


Figure 2.10 Influence on compressive strength of variation in cement and water contents at fixed total w/c ratio for concrete made with PC and different coarse aggregates

Tensile Strength

Data in Figure 2.11 indicate that variation (or reduction) in cement content at fixed free w/c ratio has little or no clear influence on tensile strength. As indicated above, compressive strength increases slightly with cement and water reduction in equal proportion and, therefore, cement reduction is likely to increase the compressive / tensile strength ratio, reducing the ductility of concrete. Therefore, it appears that potential benefits to the paste / aggregate bond through reduced bleeding, as discussed earlier, may be offset by reduced paste / aggregate ratio as there is less cement paste to cover a greater surface area of aggregate.

Static Modulus of Elasticity in Compression

There are few data available in the literature considering the role of cement content in determining elastic modulus. Figure 2.12 shows results reported for concrete mixes of fixed free w/c ratio 0.50. These show slightly higher moduli at lower cement contents, reflecting the increased compressive strength results reported by the authors.

Whilst the authors provide little discussion, it appears that as aggregate has a higher modulus of elasticity compared to the cement paste, cement-reduced concretes at fixed w/c ratio (with increased aggregate and reduced cement paste contents) result in higher elastic modulus values.

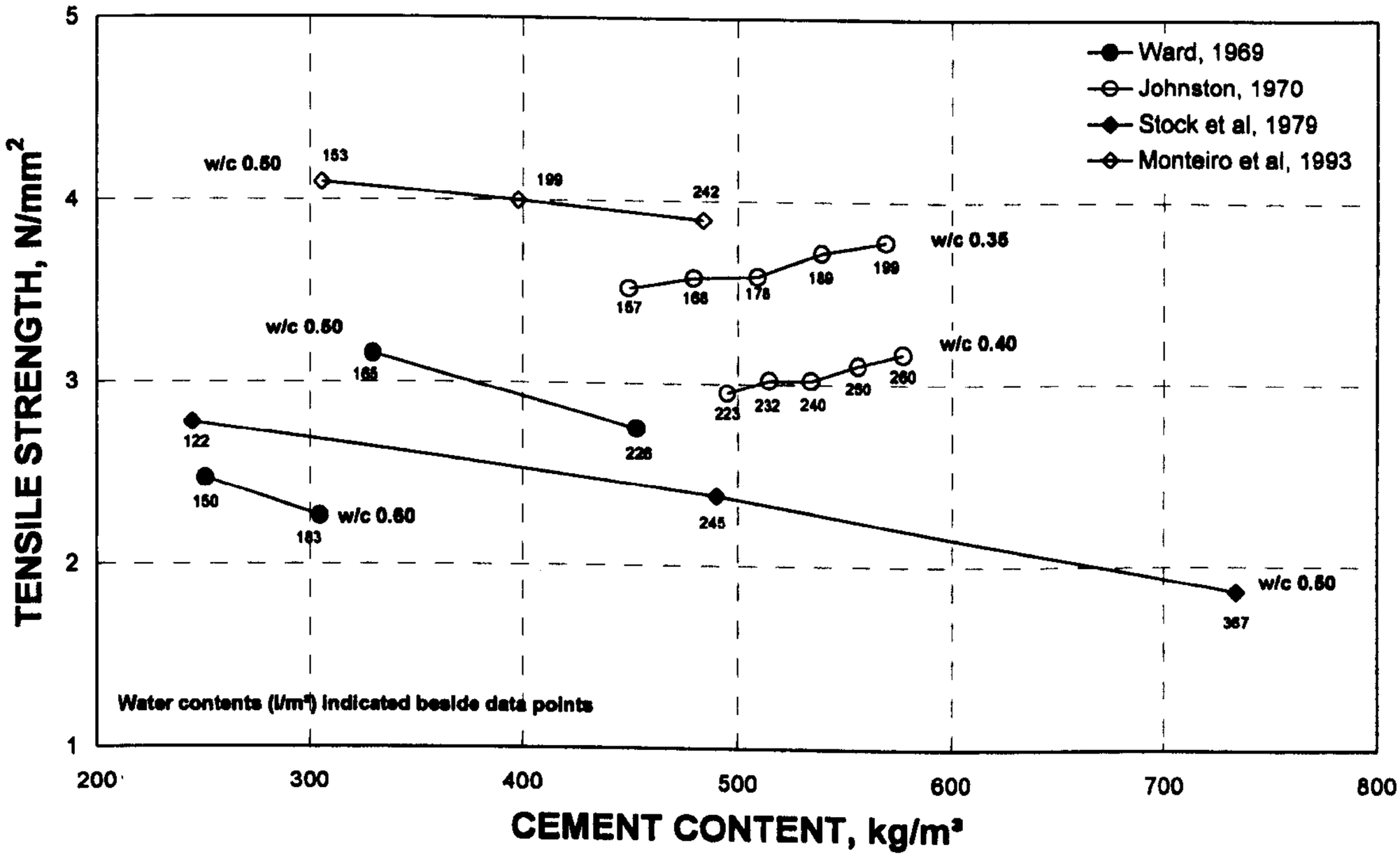


Figure 2.11 Influence on tensile strength of variation in cement and water contents at fixed free w/c ratio

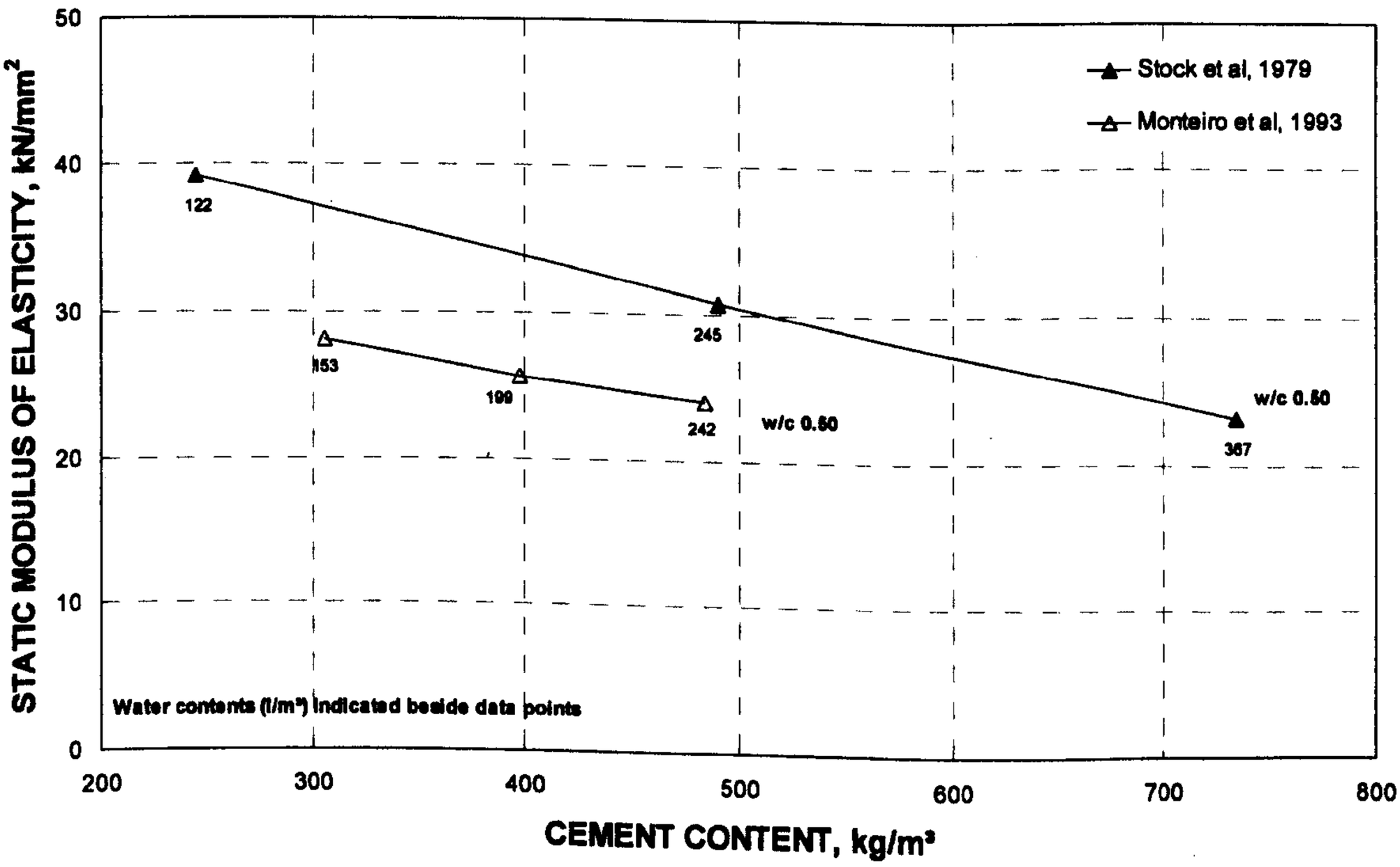


Figure 2.12 Influence on modulus of elasticity of variation in cement and water contents at fixed free w/c ratio

Drying Shrinkage

Drying shrinkage results are plotted against cement content in Figure 2.13 for concrete / mortar mixes having either fixed free (Shoya, 1979; Hansen and Almudaiheem, 1987; Bissonnette *et al*, 1999) or fixed total (Keene, 1960; Neville, 1962) w/c ratios. Comparison of data between studies is difficult, given that the water-curing and air-drying temperatures and durations varied widely. However, in all cases, at a given w/c ratio, least shrinkage occurred at lowest cement (and, therefore, water) content.

Little discussion of these data is given in the literature, but the observed behaviour is likely to be due to relative changes in the quantities of cement paste, which undergoes shrinkage and, aggregate, which has a restraining effect. In addition, for mixes having fixed total w/c ratio, reducing shrinkage with cement reduction is likely to partly reflect the increased water absorption due to higher aggregate content (*i.e.* resulted in lower free w/c ratios).

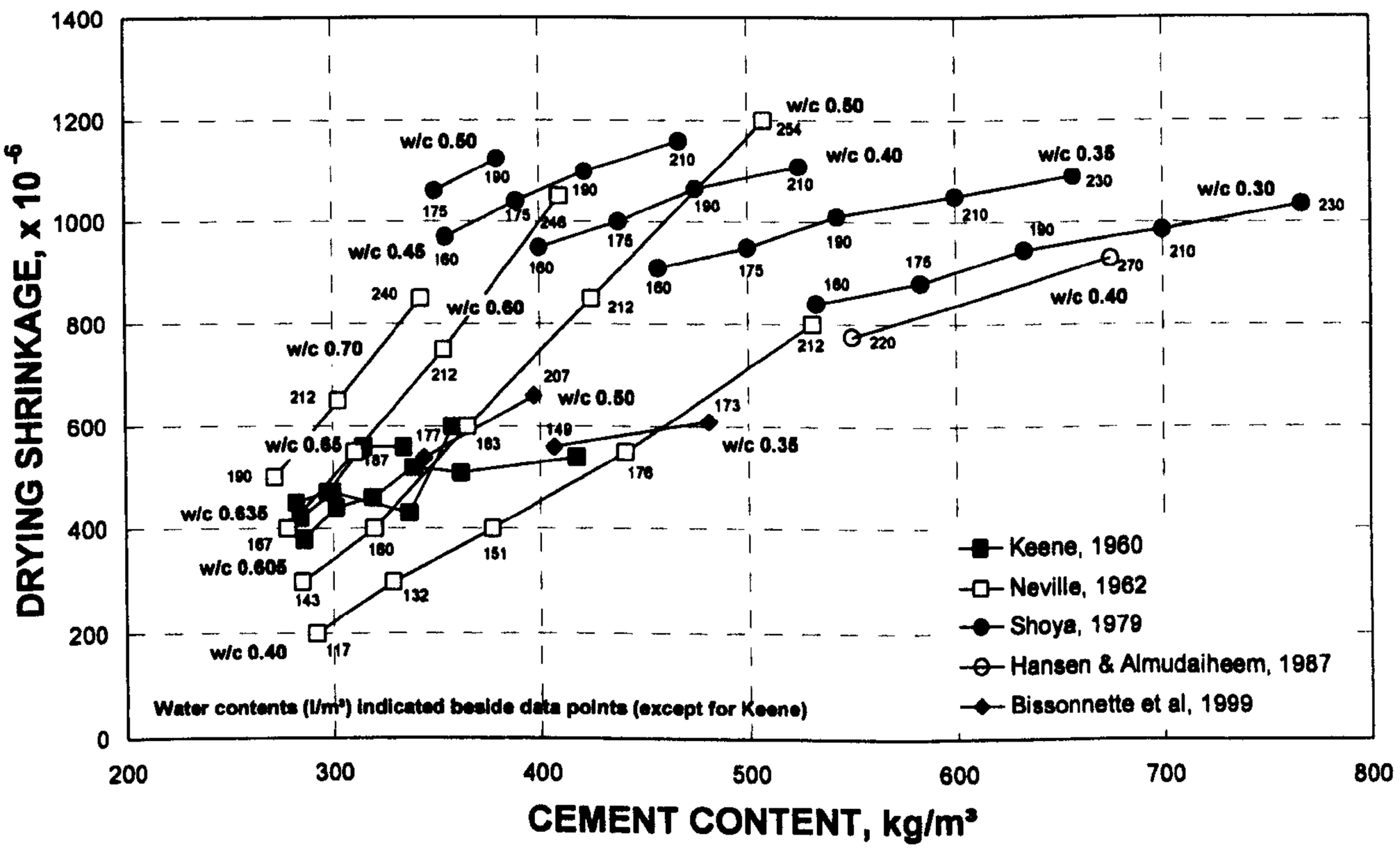


Figure 2.13 Influence on drying shrinkage of variation in cement and water contents at fixed w/c ratio

2.4.3 Permeation Properties

Absorption and Sorptivity

Water absorption and sorptivity (rate of absorption over a given period of time) results of concrete specimens made with different cement contents at fixed free (McCarter *et al*, 1992; Dias, 1993; Buenfeld and Okundi, 1998) and total (Keene, 1960) w/c ratios, are shown in Figure 2.14 and Figure 2.15, respectively. Test procedures differed between these studies. Keene (1960) measured

absorption after 10 minutes relative to the oven dry weight, whilst Buenfeld and Okundi (1998) measured the weight of absorbed water at set time intervals up to 5 days. McCarter *et al* (1992) and Dias (1993) calculated sorptivity over 25 and 49 hours, respectively. In general, variation in cement content at fixed w/c ratio had either little influence on absorption / sorptivity, or slightly lower values were reported at lowest cement content, and this trend was unaffected by cement type.

Given that cement and water reduction in equal proportion had no significant influence on the strength, the observed changes in absorption / sorptivity characteristics are due to reduced water contents and, therefore, lower voids in cement reduced mixes. In addition, examination of the split surface of specimens after testing, McCarter *et al* (1992) indicated that water moved around the coarse aggregates, suggesting that capillary suction is influenced by aggregate distribution, in addition to the porosity of the cement paste. Given this, mixes having lowest cement and water contents may be expected to exhibit least absorption / sorptivity due to reduced porosity of the cement paste, and greater restriction to capillary suction through increased aggregate content by discontinuity of the capillary pores and greater tortuosity of the flow paths. On the other hand, increased aggregate content is expected to increase the effective ITZ (aggregate-cement paste interfacial transition zone) area, which has the highest porosity of the composite. However, it appears that this effect has a negligible influence on the absorption / sorptivity of concrete, or its influence is offset by the other mechanisms indicated above.

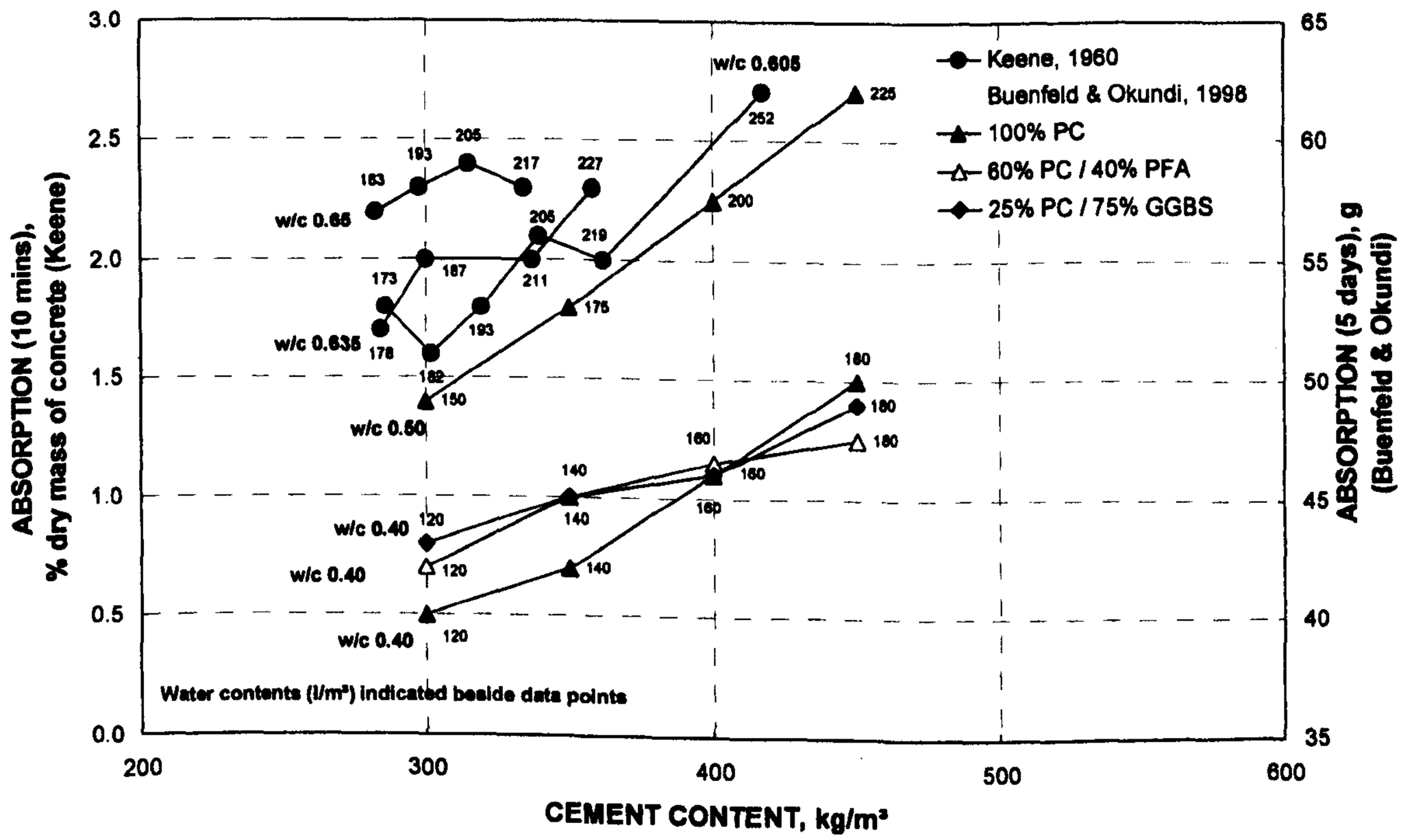


Figure 2.14 Influence on water absorption of variation in cement and water contents at fixed w/c ratio

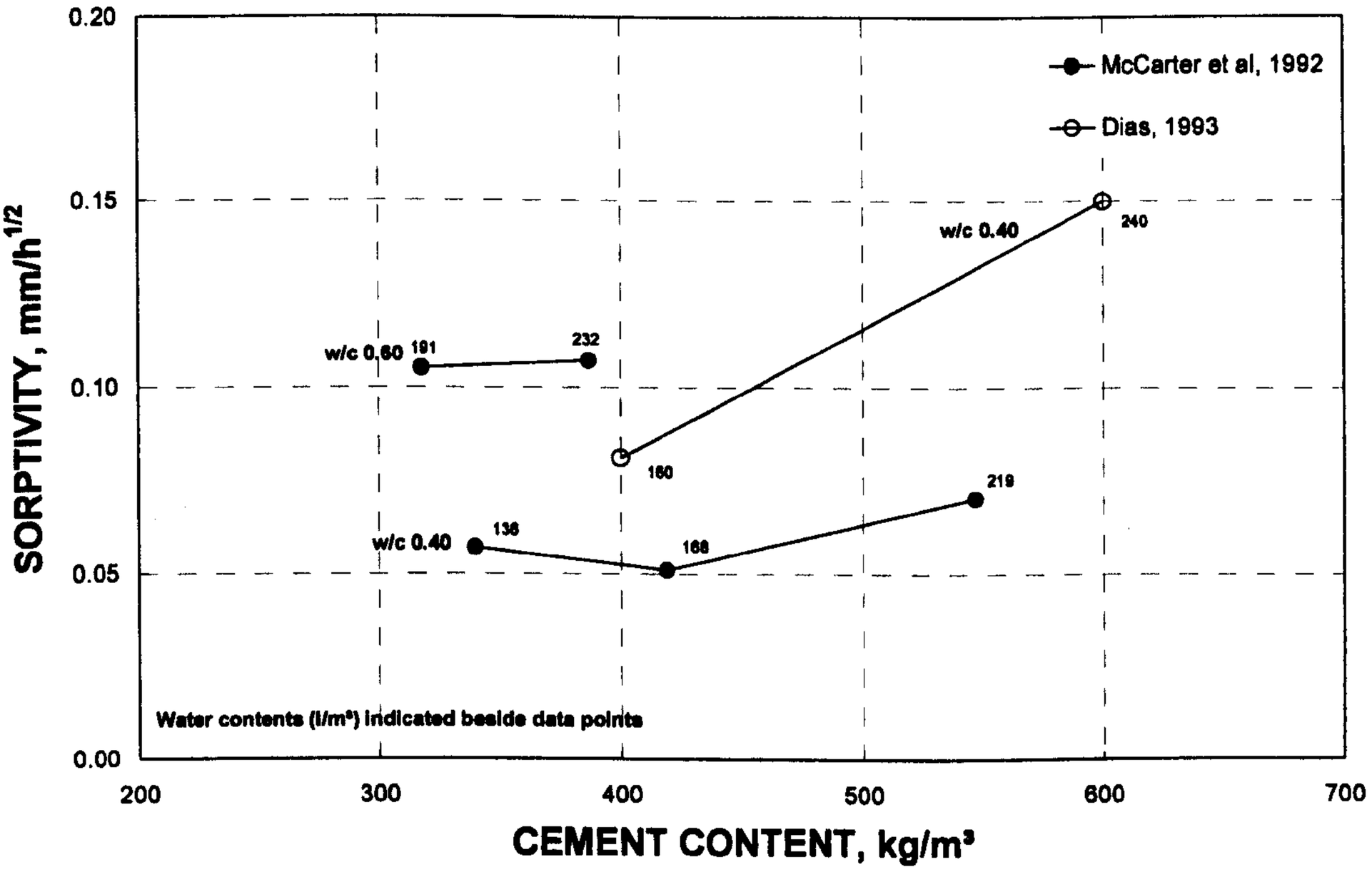


Figure 2.15 Influence on sorptivity of variation in cement and water contents at fixed free w/c ratio

Initial Surface Absorption (ISA)

Figure 2.16 shows initial surface absorption measurements made after 10 minutes (ISA-10), as described in BS 1881: Part 208 (BSI, 1996), plotted against cement content for concrete mixes having fixed free w/c ratios between 0.35 and 0.82. In all studies, at a given w/c ratio, surface absorption reduced with cement (and water) reduction. Air-cured concrete exhibited higher ISA-10 than equivalent water-cured concrete, as expected, but the influence of cement content was essentially similar between these two curing regimes (Dhir *et al*, 1987b). In addition, the inclusion of approximately 30% PFA (by weight of total cement content) in the mix led to similar behaviour when cement content was reduced at fixed w/c ratio (Dhir *et al*, 1996; McCarthy *et al*, 1996).

In most of these studies (Dhir *et al*, 1987a; Dhir *et al*, 1996; McCarthy *et al*, 1996), a superplasticizing or water-reducing admixture was used to offset the workability loss that occurs with cement and water reduction at fixed w/c ratio. As noted earlier, it has been suggested that improvement of the microstructure occurs through greater dispersion of PC flocs with the use of these admixtures. However, similar reductions in ISA-10 were obtained without chemical admixtures (Dhir *et al*, 1987b), suggesting that the dispersing effect with the former had little influence on the observed behaviour. Given that, in these studies, strength was not influenced significantly by variation in cement and water contents, the observed improvements to the microstructure with cement and water reduction are likely to be due to the reduction in the volume

of cement paste (more porous fraction) and greater restriction to capillary suction through increased aggregate content.

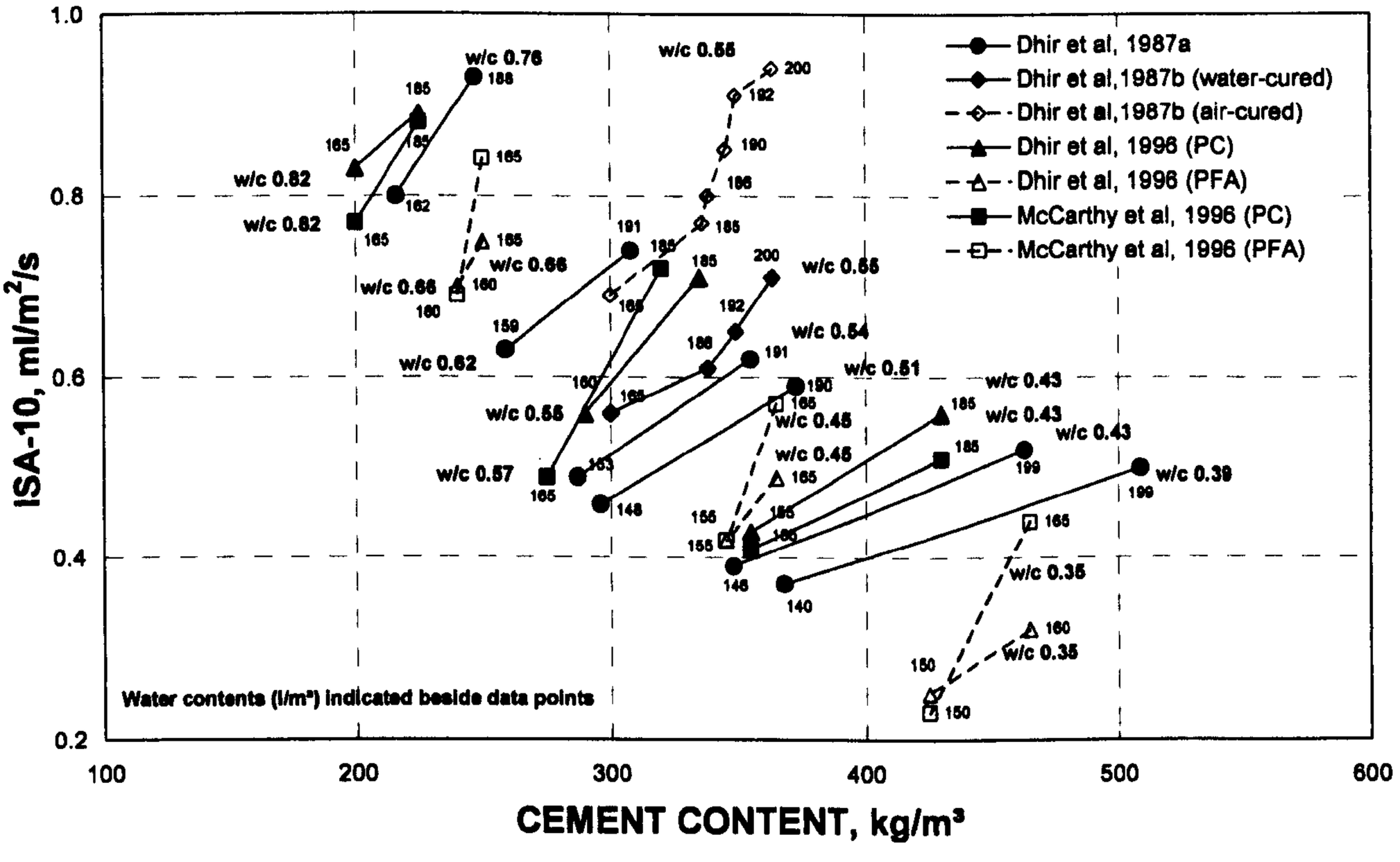


Figure 2.16 Influence on initial surface absorption of variation in cement and water contents at fixed free w/c ratio

Water, Air and Oxygen Permeability

Figure 2.17 shows water, air and oxygen permeability results plotted against cement content for concrete mixes having fixed free w/c ratio. Test procedures (namely specimen size, curing and applied air pressure during testing) differed widely between the studies. However, results exhibited essentially similar behaviour to those observed for ISA-10 and water absorption with permeability generally reducing with cement and water content. The trend was unaffected by cement type, although PC / GGBS concrete showed surprisingly higher oxygen permeability values compared to concrete made with PC and PC / PFA (Buenfeld and Okundi, 1998).

The authors give little discussion of the data or controlling mechanisms, but it is likely that mechanisms discussed earlier, also control water, air and oxygen permeability through concrete. The superplasticizing admixture used by the authors (except Buenfeld and Okundi, 1998) to maintain workability may also be a contributing factor.

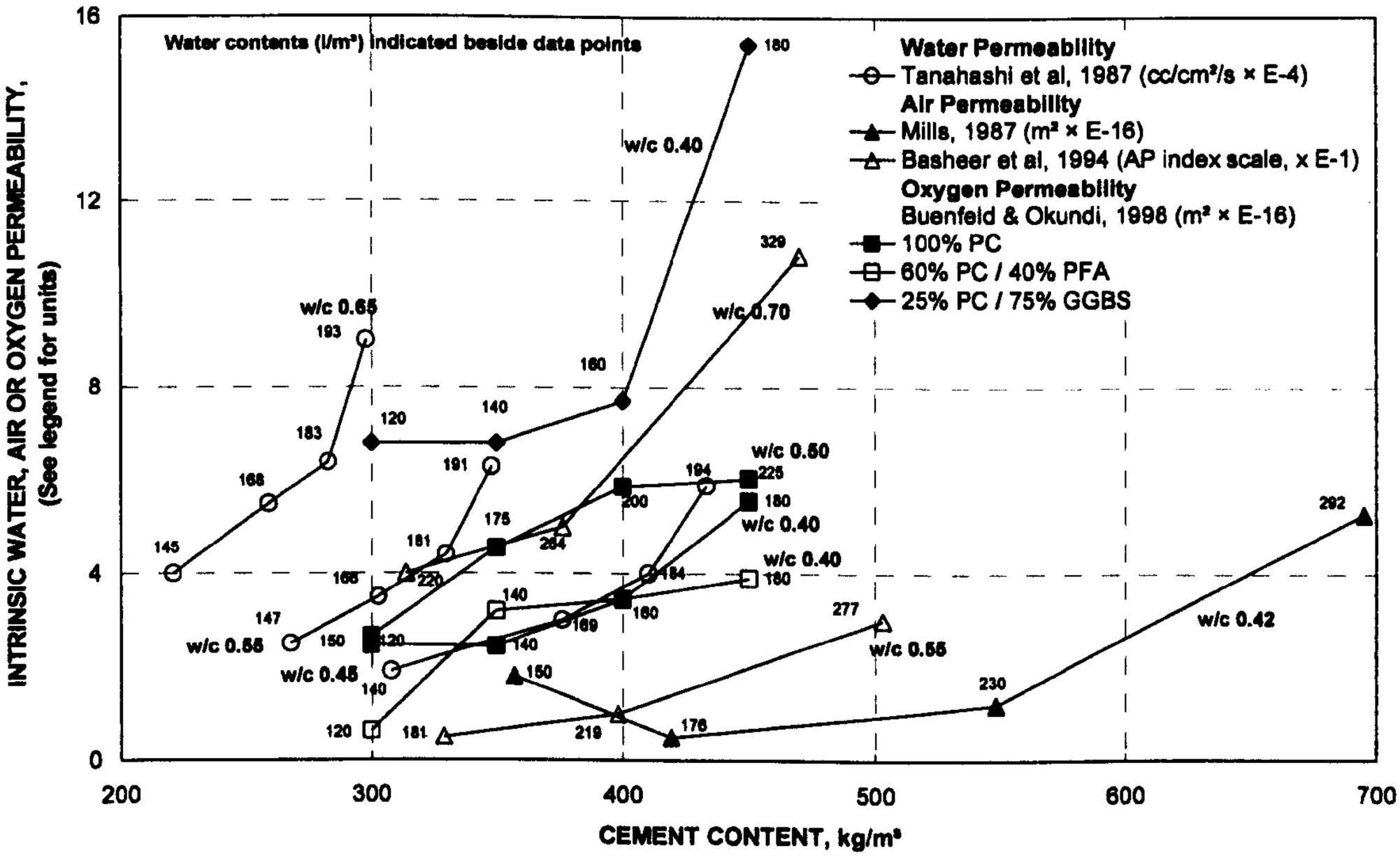


Figure 2.17 Influence on water, air and oxygen permeability of variation in cement and water contents at fixed free w/c ratio

2.4.4 Durability Properties

Carbonation Resistance

Figure 2.18 shows the influence of change in cement content at fixed free w/c ratio on carbonation depth. In all of these studies, carbonation was accelerated by higher concentrations of carbon dioxide compared to the natural environment. The results indicate that carbonation resistance was either unchanged or improved slightly with cement and water reduction. This behaviour was not influenced by curing regime (Dhir *et al*, 1989b) or cement type (Buenfeld and Okundi, 1998). In addition, Loo *et al* (1994) indicated that variation in cement and water contents in equal proportion had no significant influence on the rate of carbonation (expressed as a carbonation coefficient) for mixes having fixed free w/c ratios between 0.70 and 0.40, see Figure 2.19.

As noted previously, permeation results (Dhir *et al*, 1987a; Basheer *et al*, 1994; Buenfeld and Okundi, 1998) indicate improved microstructure with cement and water reduction in equal proportion and this is likely to be a contributing factor to the observed behaviour. In addition, in the work carried out by Dhir *et al* (1987a), enhanced performance may have been partly due to inclusion of superplasticizer in mixes having lowest cement and water contents.

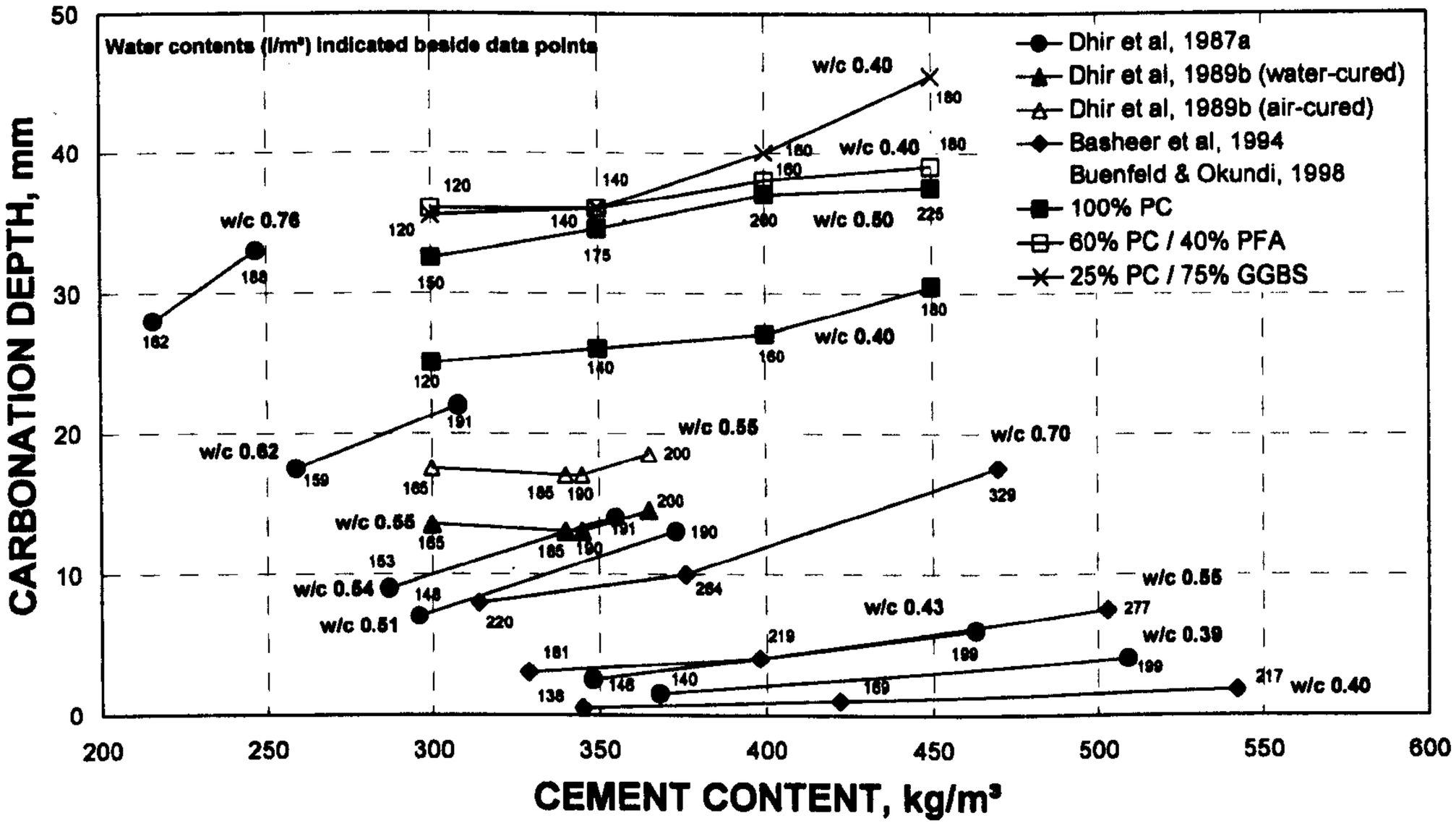


Figure 2.18 Influence on carbonation depth of variation in cement and water contents at fixed free w/c ratio

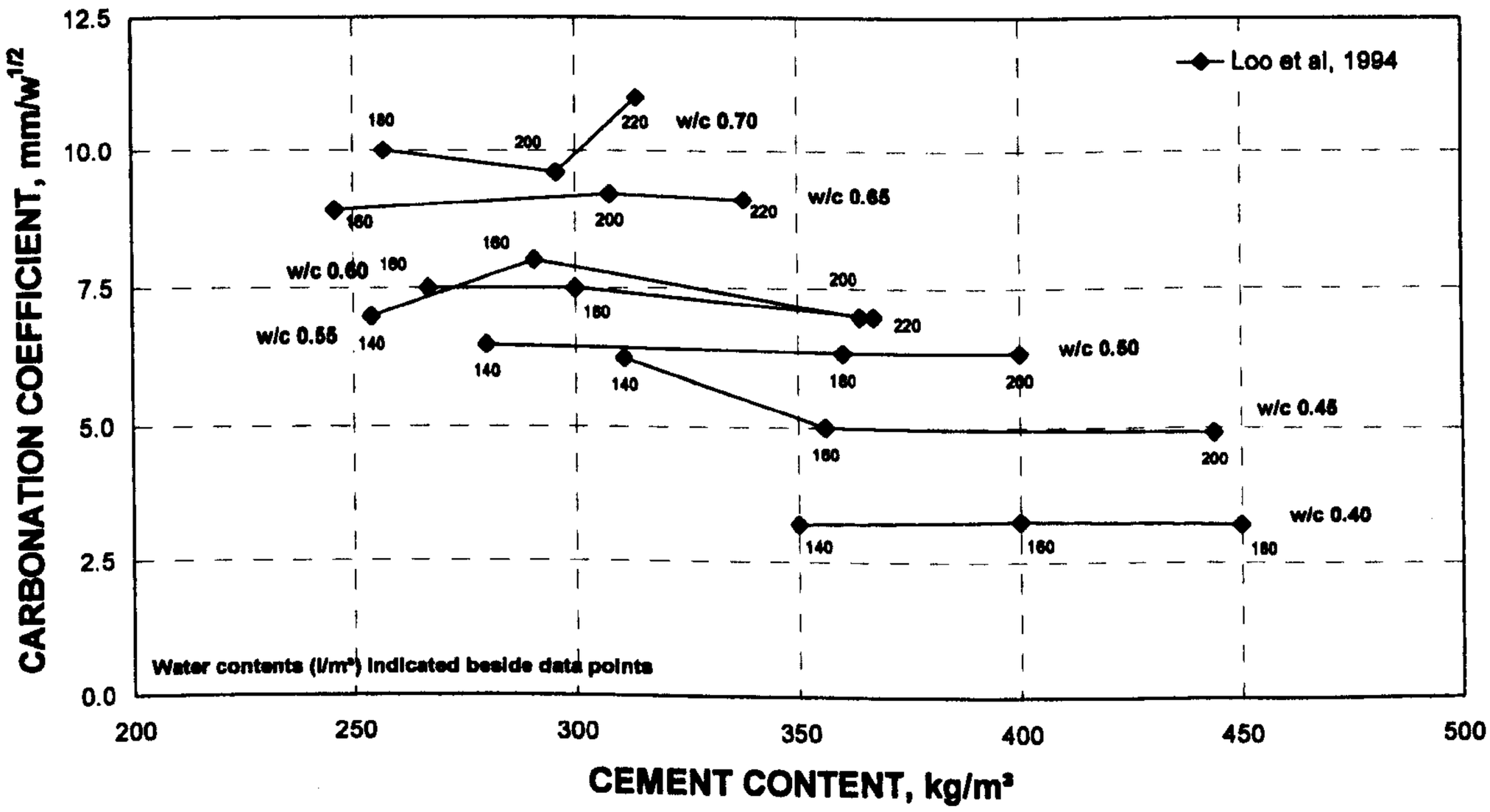


Figure 2.19 Influence on carbonation coefficient of variation in cement and water contents at fixed free w/c ratio

Chloride Resistance

Figure 2.20 shows coefficient of chloride diffusion (calculated using Fick's law) plotted against cement content for concrete specimens exposed to 5 M (molar) sodium chloride solution. Generally, at a given free w/c ratio, a reduction in cement content had little influence on the diffusion coefficient or improved it slightly. This behaviour was not particularly affected by curing regime (McCarthy *et al*, 1996) or cement type (Dhir *et al*, 1996; Buenfeld and Okundi, 1998). However, for a given mix, water-curing and use of PFA or GGBS with PC, improved the chloride resistance of concrete compared to air-curing and use of PC alone.

Given that permeation properties reported by the authors indicated improved microstructure at lowest cement content (Dhir *et al*, 1987a; Dhir *et al*, 1996; McCarthy *et al*, 1996; Buenfeld and Okundi, 1998), it is, perhaps, surprising that improved resistance to chloride attack was not observed in all cases. The observed behaviour with cement and water reduction in equal proportion appears to be a balance between reduced chloride binding capacity due to the lower cement content and improved microstructure (Dhir *et al*, 1996; McCarthy *et al*, 1996).

Other studies measuring the chloride content (at or near the concrete surface) plotted against cement content for specimens exposed to different chloride exposure conditions (see Appendix A for details), are shown in Figure 2.21. It appears that a reduction in cement content at fixed free w/c ratio had little or no clear influence on the measured chloride contents at or near the concrete surface. Dias (1993) suggested that improved performance of cement and water reduced concrete was due to reduced microcracking (due to less shrinkage) and moisture transport (due to lower paste content).

Sulfate Resistance

Limited experiments have been carried out to examine the role of cement content in determining the sulfate resistance of concrete mixes having fixed w/c ratio. Figure 2.22 shows residual strengths (expressed as a percentage of continuously water-cured specimens) plotted against cement content for concrete specimens exposed to solutions of either 0.5% by mass SO_3 (sulfite) for 12 months (Keene, 1960) or 5000 ppm SO_4^{2-} (sulfate) for 90 days (Kumar and Rao, 1995). Residual strengths of approximately 95 and 90% were reported over the range of cement contents, tested by Keene (1960) and Kumar and Rao (1995), respectively. Thus, from the available data, the reduction in cement content at fixed w/c ratio appears to have no significant influence on sulfate resistance of concrete.

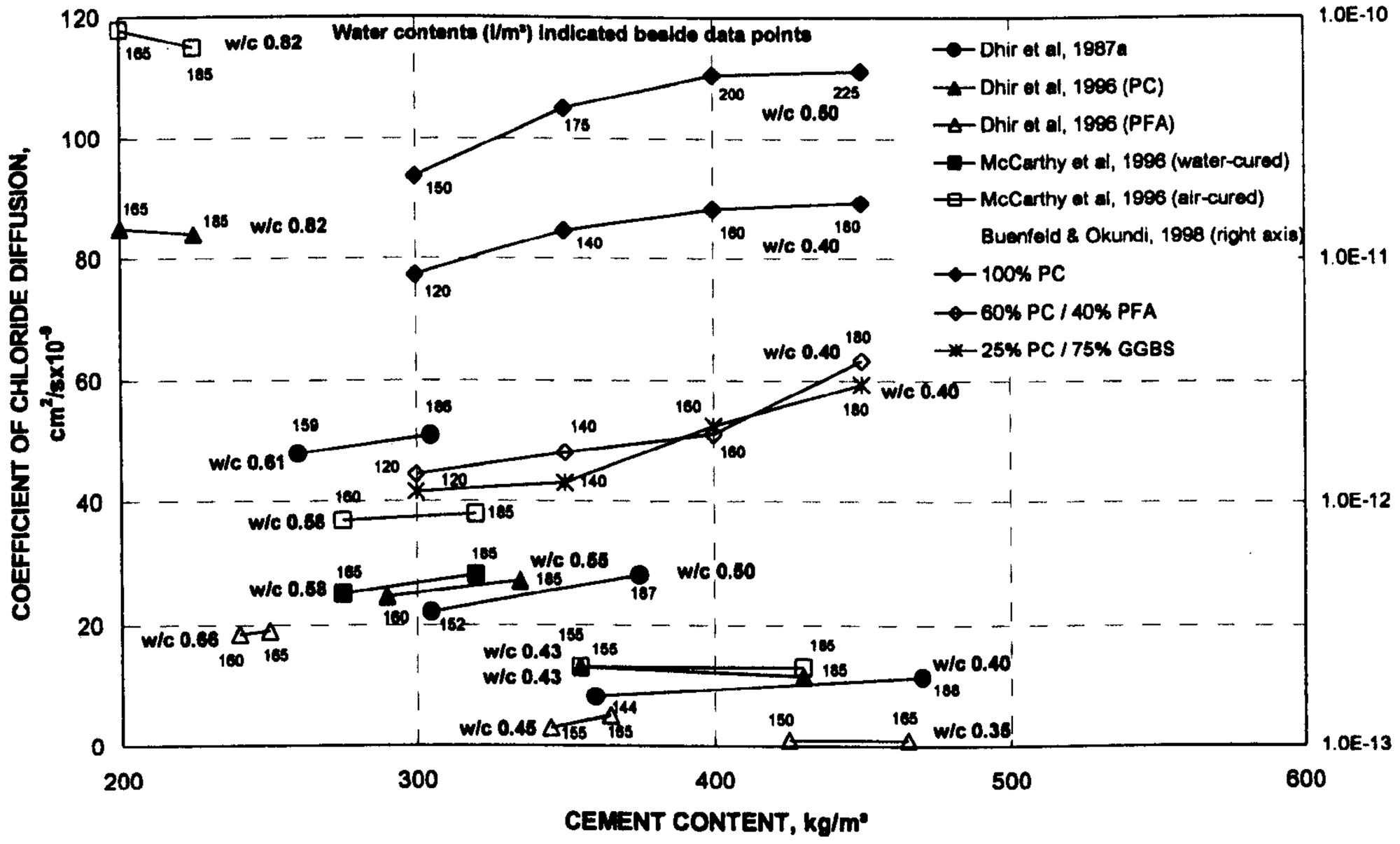


Figure 2.20 Influence on chloride diffusion coefficient of variation in cement and water contents at fixed free w/c ratio

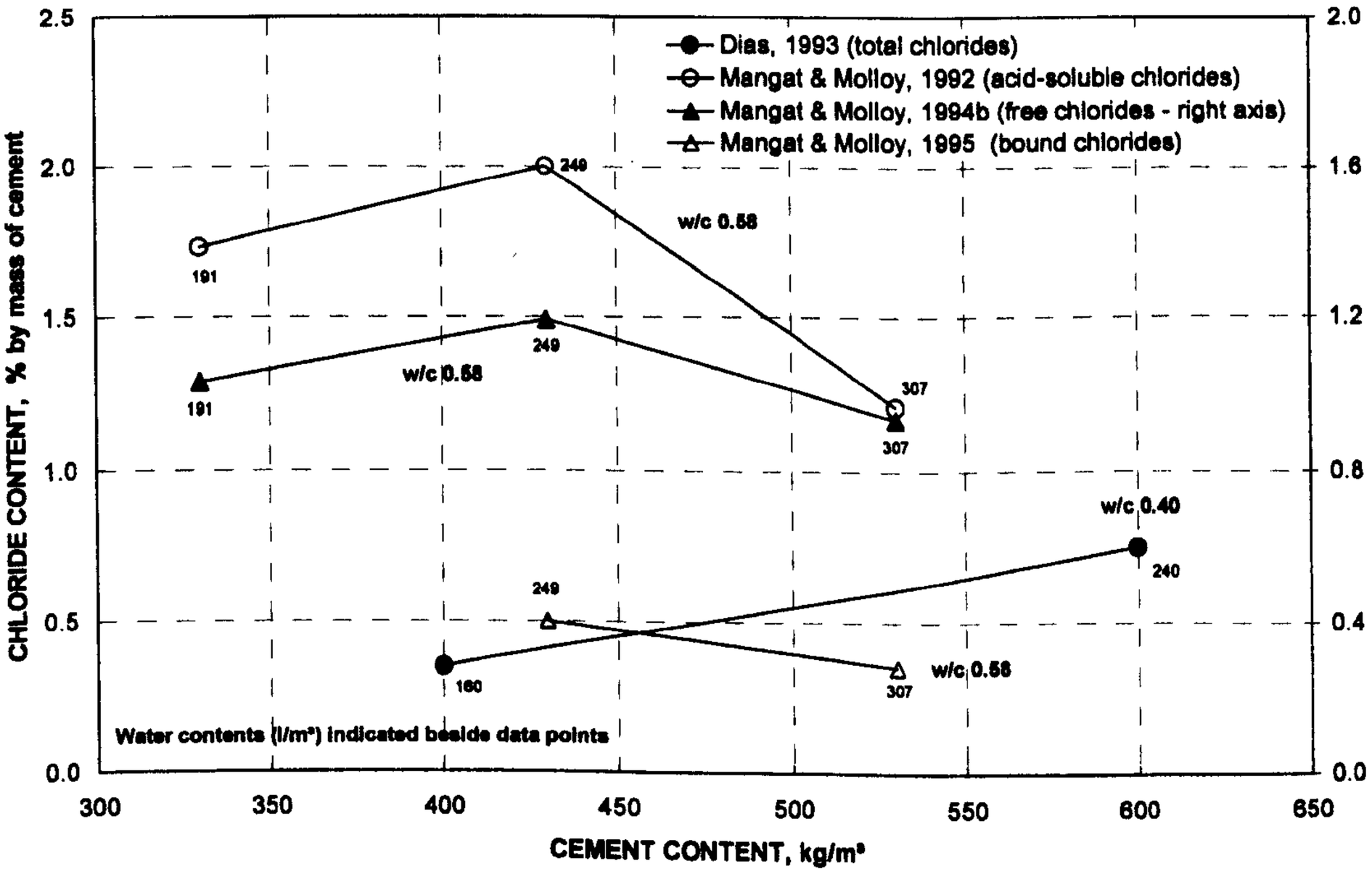


Figure 2.21 Influence on chloride content of variation in cement and water contents at fixed free w/c ratio

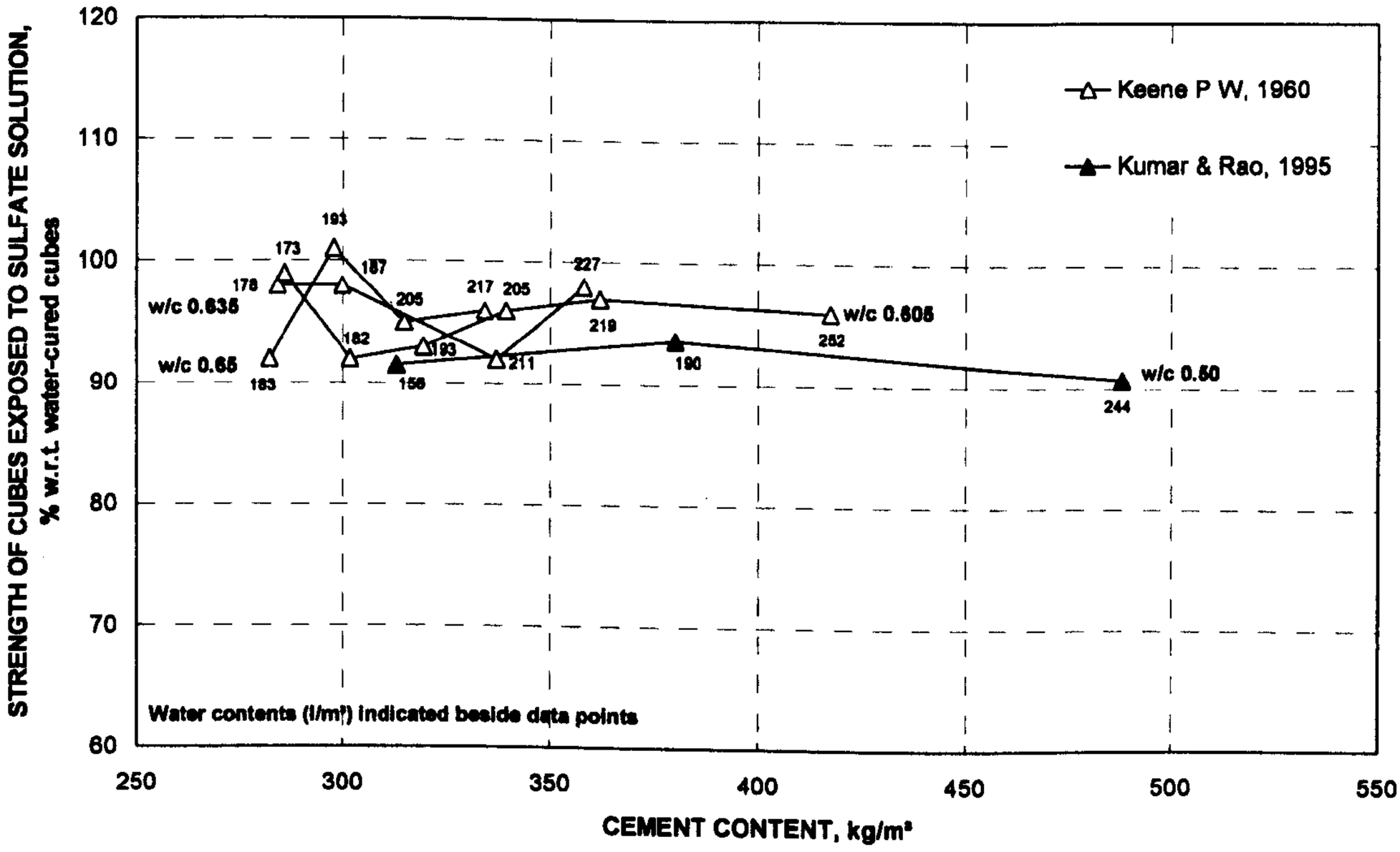


Figure 2.22 Influence on sulfate resistance of variation in cement and water contents at fixed w/c ratio

Freeze / Thaw Resistance

In literature, freeze / thaw resistance of concrete has been tested using specified failure criterion or fixed exposure period. Figure 2.23 shows the number of freeze / thaw cycles required to achieve failure, plotted against cement content for concrete mixes having fixed total (Keene, 1960) or free (Dhir *et al*, 1987a) w/c ratio. Keene (1960) carried out tests involving freezing in water and thawing in air with failure defined as 5% mass loss, whilst Dhir *et al* (1987a) carried out freezing in air and thawing in water with failure defined as linear expansion exceeding 300×10^{-5}.

Under fixed exposure period, results from tests carried out on concrete specimens exposed to a predetermined number of freeze / thaw cycles, plotted against cement content at fixed free w/c ratio, are shown in Figure 2.24.

It appears that a reduction in cement content at fixed w/c ratio had either little or no clear influence on freeze / thaw resistance of concrete (Keene, 1960) or else improved it slightly (Dhir *et al*, 1987a; Basheer *et al*, 1994).

Given that Dhir *et al* (1987a) found that strength was not influenced significantly by variation in cement content at fixed w/c ratio, the authors suggested that the improved freeze / thaw resistance noted for mixes having lowest cement content at a given w/c ratio, may have been partly due to the 0.7% increase in entrained air through use of the superplasticizing admixture to offset workability

loss. From the available data, it appears that reduced free water content (lower expansion forces on freezing) and increased air content in cement-and-water-reduced mixes may contribute to improve the freeze / thaw resistance of concrete.

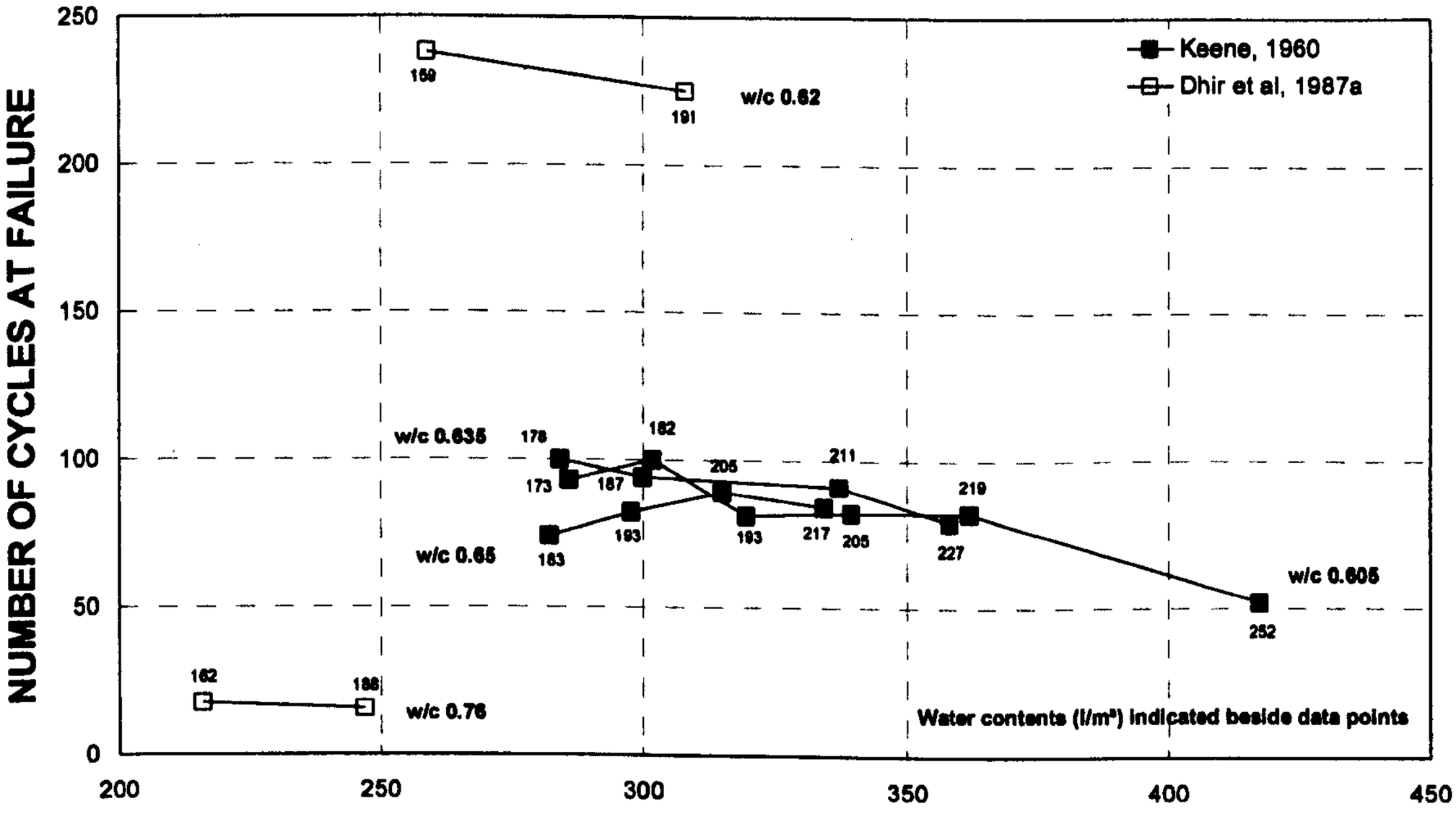


Figure 2.23 Influence on freeze / thaw resistance of variation in cement and water contents at fixed w/c ratio (specified failure criterion)

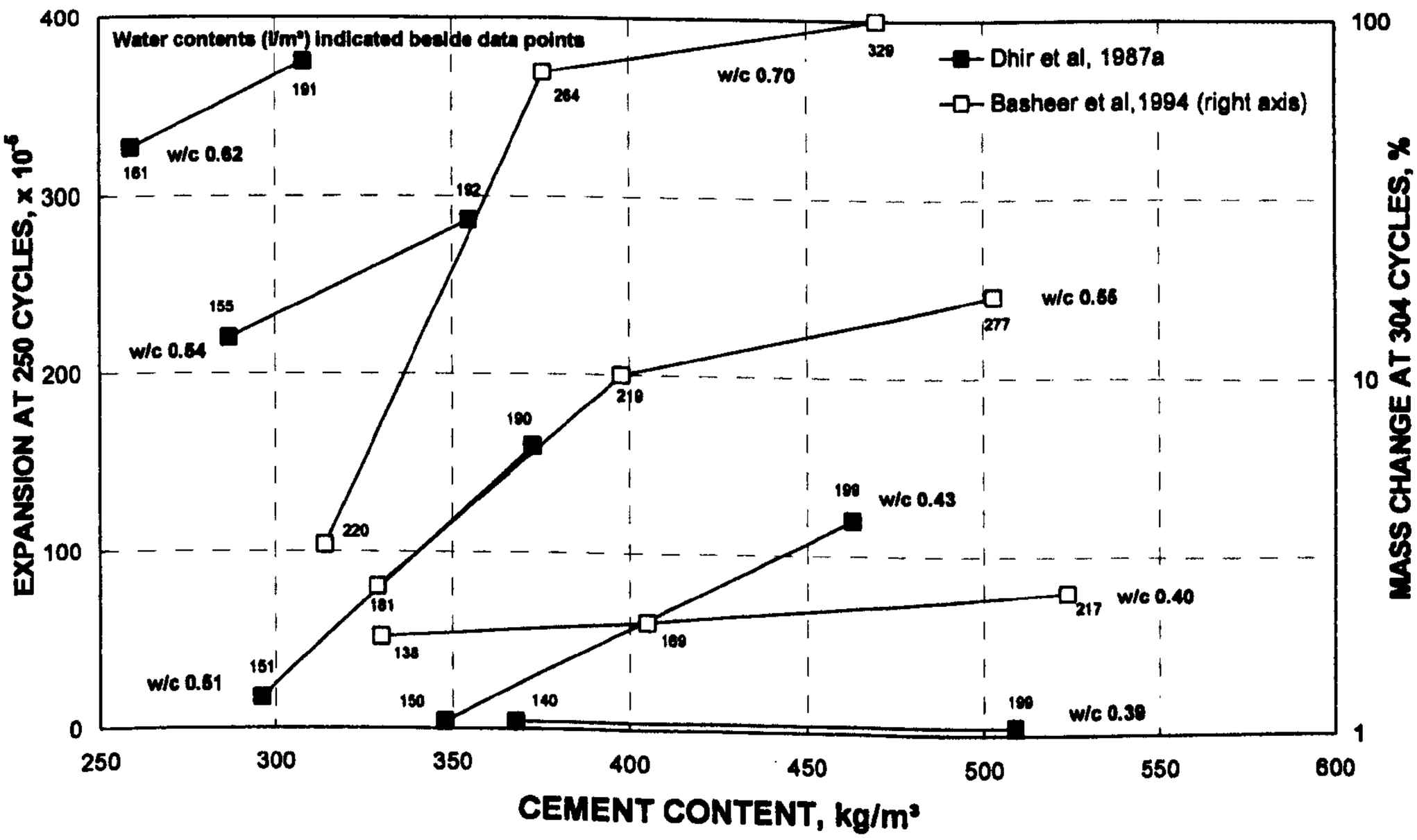


Figure 2.24 Influence on freeze / thaw resistance of variation in cement and water contents at fixed free w/c ratio (fixed exposure period)

Abrasion Resistance

Abrasion depth measurements made using a modified BCA method on concrete specimens having fixed free w/c ratio 0.55, plotted against cement content, are shown in Figure 2.25. With variation in cement content between 365 and 300 kg/m³ (water content 201 to 165 l/m³), abrasion depths differed by up to 0.19 mm with highest resistance observed at lowest cement (and water) content.

Given that in this study (Dhir *et al* (1991)), strength was not affected by variation in cement and water contents in equal proportion, the authors suggested that mixes with reduced paste volume, *i.e.* lower cement content, exhibited improved resistance to abrasion since more aggregates were present near the concrete surface. In addition, the lower workability of mixes having least cement and water contents with associated reduced bleeding and damage to the concrete surface may have also contributed to the improved abrasion resistance.

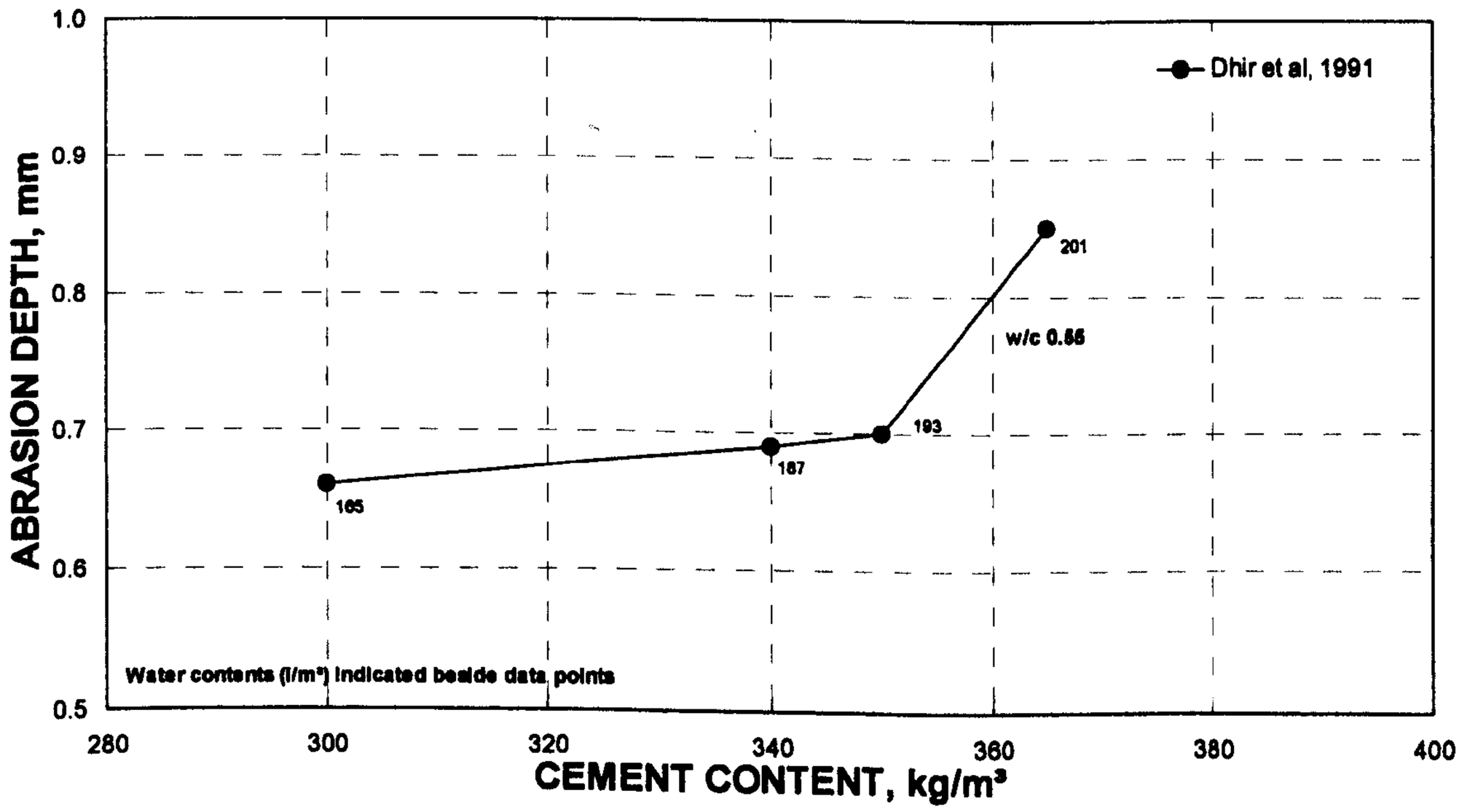


Figure 2.25 Influence on abrasion resistance of variation in cement and water contents at fixed free w/c ratio

2.4.5 Resistance to Reinforcement Corrosion

From the discussions in earlier sections, it appears that reduction in cement content at fixed w/c ratio is not, in the main, detrimental to fresh and hardened concrete properties and may improve the performance in some cases, *e.g.* compressive strength. However, it is important to note that the parameters controlling strength are not completely identical to those controlling durability and, in particular, resistance of concrete to reinforcement corrosion (De Shutter, 1999).

There are no available data considering the influence of variation in cement content at fixed w/c ratio on carbonation-induced reinforcement corrosion. However, limited work have been reported on the role of cement content on resistance of concrete to chloride-induced reinforcement corrosion.

Figures 2.26, 2.27 and 2.28 show the findings of three studies on the effect of variation in cement content at fixed free w/c ratio on resistance of concrete to chloride-induced reinforcement corrosion. Maslehuddin *et al* (1987) investigated corrosion using concrete mixes made with 100% PC and 80% PC / 20% PFA (by weight of total cement content) and limestone coarse aggregate, at fixed free w/c ratio 0.45. Total cement contents were varied from 275 to 450 kg/m^3 and specimens were partially immersed in 5% sodium chloride solution for up to 1000 days. Reported corrosion potentials after 1000 days exposure varied between -524 and -590 mV for PC concrete and between -472 and -500 mV for PC / PFA concrete (with reference to saturated calomel electrode). Corrosion rates varied between 48.5 and 50.8 μm/year for PC concrete and between 15.5 and 23.6 μm/year for PC / PFA concrete. In addition, times to corrosion initiation (based on corrosion potential values) varied between 75 and 195 days for PC concrete and between 95 and 250 days for PC / PFA concrete. Generally, different trends were obtained between corrosion potentials, corrosion rates and times to corrosion initiation, possibly due to high fluctuations in corrosion results, as usual. However, corrosion rates after 1000 days exposure, plotted against cement content, indicate that reduction in cement content of both PC and PC / PFA concrete at fixed free w/c ratio was not generally detrimental to long-term corrosion resistance. The authors gave no explanation to the observed results. However, the observed behaviour appears to be a balance between reduced chloride binding capacity due to lower cement contents and improved microstructure (which controls the availability of oxygen and moisture).

In contrast, very similar experimental work (using concrete made with PC and limestone coarse aggregate) reported by Rasheeduzzafar *et al* (1987) suggests that reducing cement content at fixed free w/c ratio 0.45 was detrimental to the resistance of concrete to reinforcement corrosion (based on corrosion potential values). Cement contents were varied from 330 to 480 kg/m^3 and specimens were partially immersed in 5% sodium chloride solution for up to 500 days. After 500 days accelerated exposure, corrosion potential values varied between -360 and -450 mV (with reference to saturated calomel electrode). Based on corrosion potential values, calculated time to corrosion initiation increased by approximately 1.5 times (from 145 to 210 days) when the cement content was increased from 330 to 480 kg/m^3. A similar result has been observed by Maslehuddin *et al* (1987) for PC concrete, where time to corrosion initiation increased by a factor of 2.6 (from 75 to 195 days) when the cement content was increased from 275 to 450 kg/m^3. The authors suggest that the poor corrosion resistance of cement-and-water-reduced concrete mixes was due to decreasing

chloride binding capacity. However, both of these investigations gave neither chloride diffusion coefficients nor chloride content values.

Mangat and Molloy (1992) tested the resistance of concrete made with PC and crushed granite coarse aggregate to chloride-induced reinforcement corrosion at fixed free w/c ratio 0.58. They varied the cement content from 330 to 530 kg/m^3 and specimens were exposed to alternating six hours periods of spraying with sea water and drying in air for up to about 600 days. After 520 days exposure, corrosion potentials for mixes having cement contents 330, 430 and 530 kg/m^3 were -515, -508 and -538 mV (with reference to saturated calomel electrode), respectively. Corresponding corrosion rates at the same exposure period were 7.2, 7.5 and 6.0 μm/year for mixes with cement contents 330, 430 and 530 kg/m^3, respectively. Measured acid-soluble chloride ion concentrations at the level of rebar reflected the corrosion rates (see Section Chloride Resistance). Altogether, it appears that changes occurring with cement reduction were very small and possibly negligible. The authors suggest that the cement content had an insignificant influence on corrosion resistance of concrete, w/c ratio being the main controlling factor.

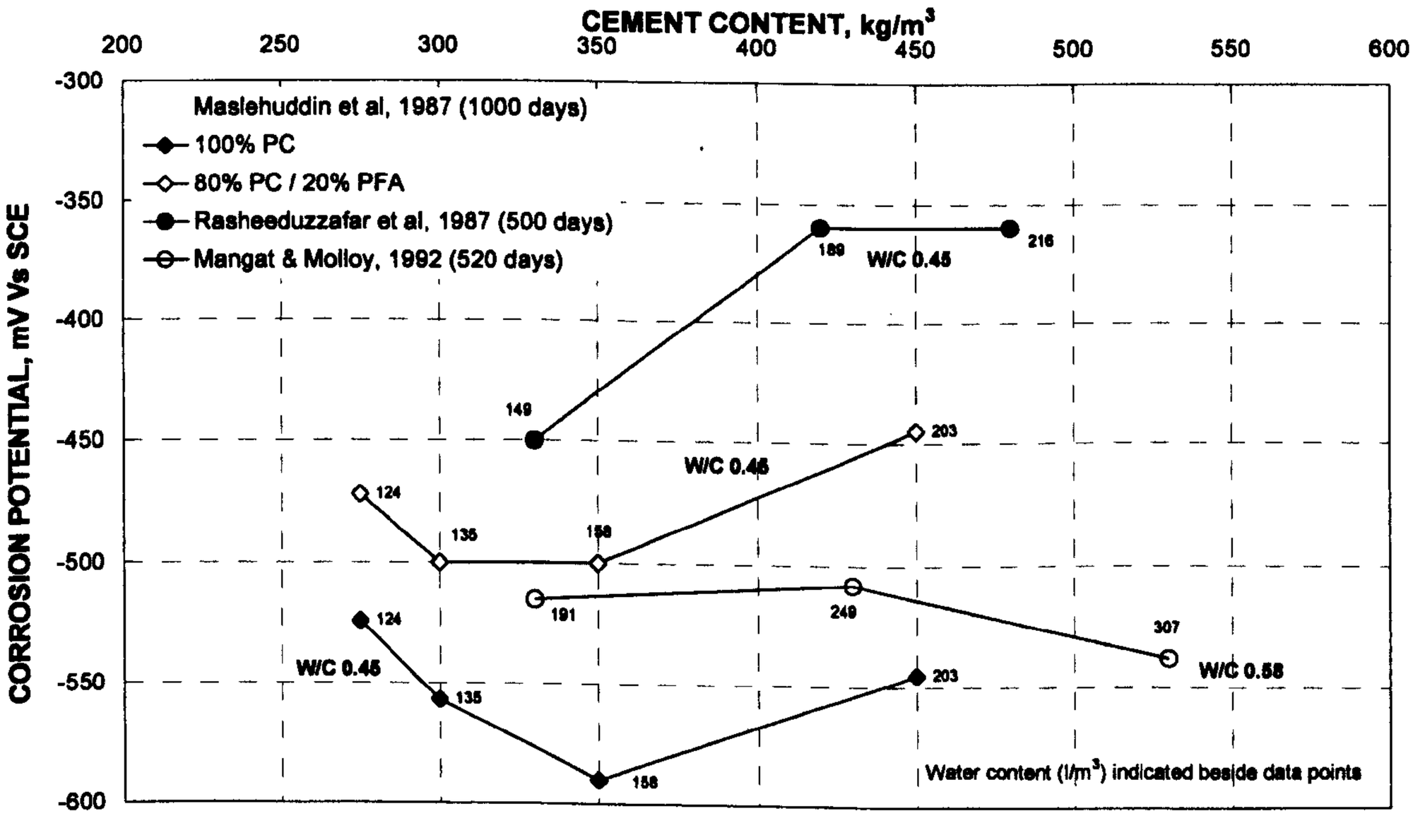


Figure 2.26 Influence on corrosion potential of variation in cement and water contents at fixed free w/c ratio

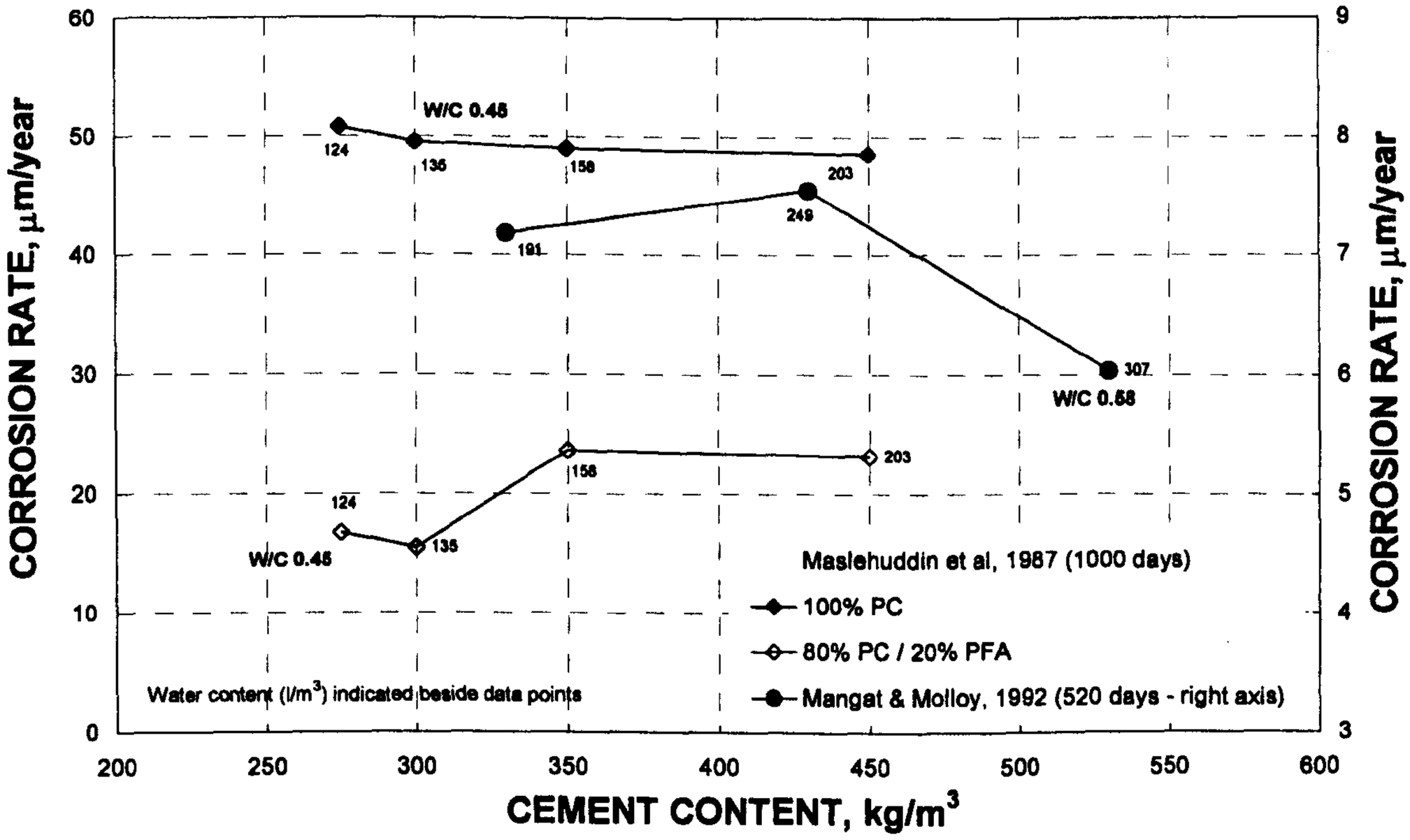


Figure 2.27 Influence on corrosion rate of variation in cement and water contents at fixed free w/c ratio

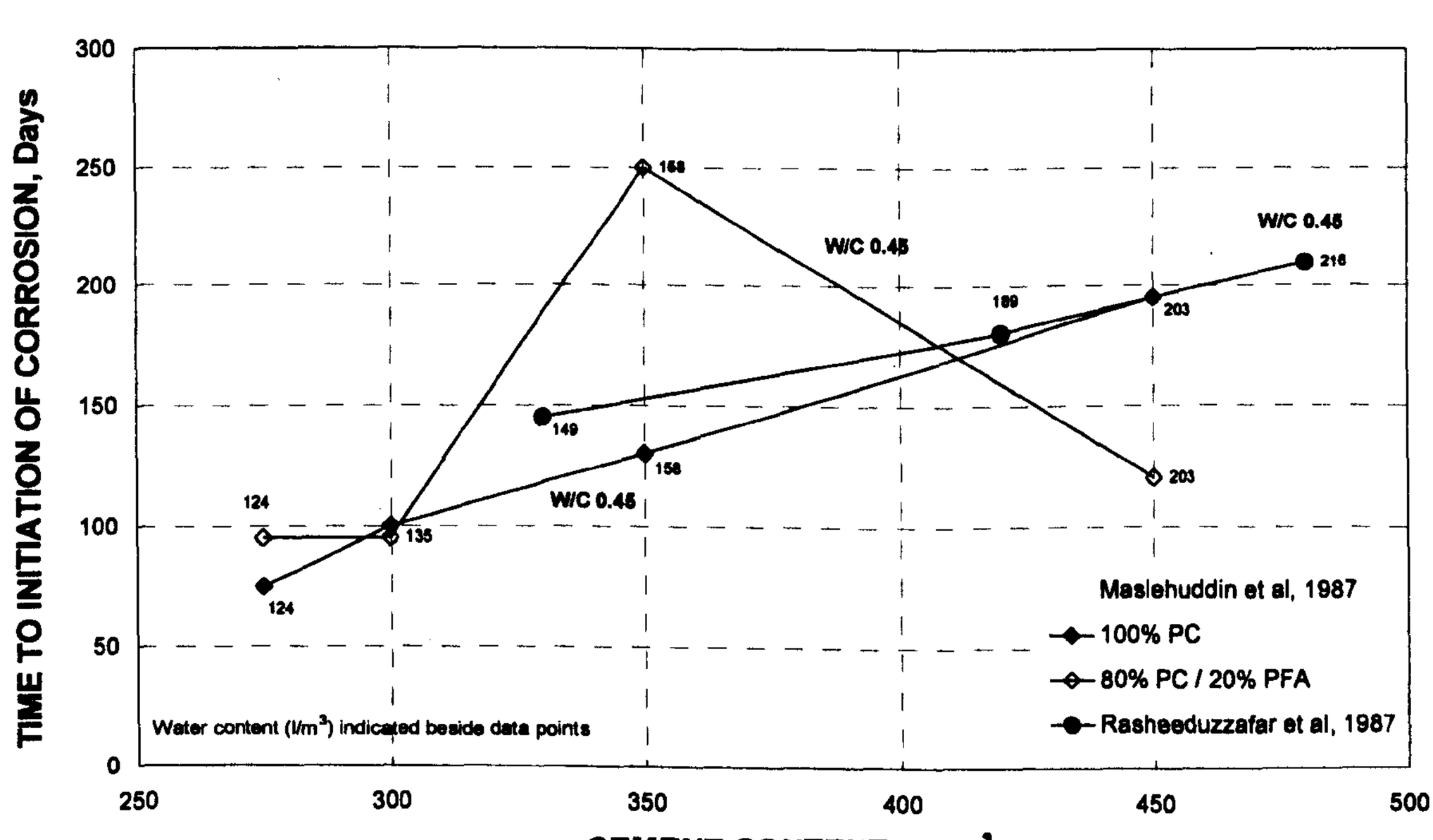


Figure 2.28 Influence on time to corrosion initiation of variation in cement and water contents at fixed free w/c ratio

It should be noted that corrosion potential indicates corrosion condition (or corrosion risk) and it is not safe to formulate conclusions concerning corrosion activity of embedded steel in concrete only using potential values (ASTM C 876, 1991; Broomfield, 1997). Given that permeation properties

(which influence the rate of corrosion, once initiated) indicate improved microstructure at lowest cement content, it is, perhaps, surprising that improved resistance to reinforcement corrosion was not observed in cement-reduced mixes made at fixed w/c ratio. In addition, Buenfeld and Okundi (1998) suggest that electrical conductivity, which has an influence on the rate of corrosion, was either unaffected or decreased slightly with decreasing cement content at fixed w/c ratio. Thus, based on the data available, it appears that at a given w/c ratio, cement reduction has either little or no clear influence on the resistance of concrete to reinforcement corrosion.

2.5 SUMMARY

Over the past 50 plus years, there has been significant development in the understanding of concrete durability under different exposure conditions. This has resulted in improvements in the classification of exposures as well as introduction and development of limiting mix parameters, *i.e.* maximum w/c ratio, minimum strength grade and minimum cement content, to ensure durability of concrete in UK specifications. The minimum cement contents specified in other European countries vary considerably, while in some European countries and the USA, specifications do not include minimum cement contents and, instead, rely on maximum w/c ratios and/or minimum strength grades. Therefore, the inclusion of minimum cement as a limiting mix design parameter is an issue that needs to be addressed. In other words, once the specified maximum w/c ratio (consequently the strength of concrete) is set, the influence of reduction in cement content below the specified minimum cement contents in specifications on concrete performance needs to be addressed.

It was found that insufficient data exist to establish relationships between cement content and resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion. Indeed, no data were found on the role of cement content at fixed w/c ratio on carbonation-induced reinforcement corrosion in concrete. The limited available data on the influence of variation in cement content at fixed w/c ratio on chloride-induced reinforcement corrosion in concrete are not enough to make satisfactory conclusions. Furthermore, no data exist on the influence of variation in cement content at fixed w/c ratio on resistance of cracked concrete (which represents real conditions in concrete structures) to reinforcement corrosion.

The main findings from the literature review are summarised in Table 2.5. In general, this indicates that;

- At fixed w/c ratio, cement reduction is not mainly detrimental to fresh, engineering, permeation and durability properties of concrete and may improve performance in some cases.
- There may be scope for rationalisation of mix design limitations for durability of concrete, as there seems to be little justification for specifying minimum cement contents.

However, it should be noted that cement content variations in some cases are relatively small and do not cover an adequate range below and above the specified minimum cement contents in current standards. In addition, many of the studies allowed workability to fall as cement (and water) content was reduced at fixed w/c ratio and this does not represent concrete mixes, which are practical.

Table 2.5 Summary of the influence of cement content on the properties of concrete (reported in the literature)

CONCRETE PROPERTY	INFLUENCE OF REDUCTION IN CEMENT CONTENT AT FIXED W/C RATIO
Fresh Properties	
Workability	Reduces, unless water-reducing or plasticizing admixture used
Other Properties	Reduces bleeding (significantly) and temperature rise
Engineering Properties	
Compressive Strength	Little effect or slight gain
Tensile Strength	No clear effect
Static Modulus of Elasticity	Increases slightly
Drying Shrinkage	Reduces significantly
Permeation Properties	
Water Absorption and Sorptivity	Reduces generally
Initial Surface Absorption (ISA)	Reduces significantly
Water, Air and Oxygen Permeability	Reduces significantly
Durability Properties	
Carbonation Resistance	Little effect or improves slightly
Chloride Resistance	Little effect or no clear effect
Sulfate Resistance	No clear effect
Freeze / Thaw Resistance	Little effect or increases slightly
Abrasion Resistance	Increases slightly
Resistance to Corrosion	
Carbonation-Induced Corrosion	No reported data
Chloride-Induced Corrosion	Little or no clear effect

CHAPTER 3

EXPERIMENTAL DETAILS, MATERIAL PROPERTIES AND TEST PROCEDURES

3.1 INTRODUCTION

The main objective of the work was to examine the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion and permeation characteristics of concrete. For this investigation, concrete made with a range of coarse aggregate (natural gravel, granite and dolomitic magnesium limestone) and cement (100% PC, 70% PC and 30% PFA, 50% PC and 50% GGBS) types was used to ensure that the range of material properties and qualities currently in use, was covered.

In addition to resistance of concrete to reinforcement corrosion, fresh and hardened properties of concrete are important factors influencing the performance of concrete in structures. Moreover, the change in cement content at fixed w/c ratio correspondingly changes the total aggregate content. Therefore, the performance of concrete is likely to depend on aggregate quality in addition to the quality of cement paste and, thus, the study also gave attention to the use of high porosity (high water absorption) coarse aggregates having relatively low resistance to pulverisation (lower impact resistance and crushing resistance). Indeed, considering the combined influences of cement content and coarse aggregate characteristics in determining the performance of concrete, in this work, concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate (the major cement and coarse aggregate types used for the project) was used to examine the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the fresh, engineering, permeation and durability properties.

3.2 EXPERIMENTAL PROGRAMME

For practical convenience, the experimental programme was carried out in three stages.

Stage 1

This stage investigated the effect of change in cement content at fixed w/c ratio on the fresh, engineering, permeation and durability properties of concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate.

In this work, a series of mixes was designed with a wide range of w/c ratios given in BS 5328: Part 1 (BSI, 1997) and covered a range of cement contents above and below the minimum cement contents given in BS 5328: Part 1.

The outline of the experimental programme of Stage 1 is presented in Figure 3.1. It shows the w/c ratios that each property was tested (where no w/c is given, the property was tested for all four w/c ratios, 0.65, 0.55, 0.50 and 0.45).

At each w/c ratio, a Reference Mix (M1) was designed to have a workability of 75 mm nominal slump without superplasticizing admixture. Its water content was chosen to be 185 l/m^3 from previous experience and trial mixing. The effect of change in cement content at fixed w/c ratio on the performance of concrete was examined through variation in cement and water contents in equal proportions compared to the Reference Mix (M1). As the cement and water contents changed, the total aggregate content was adjusted to maintain concrete yield. At each w/c ratio, the water content was reduced in two 20 l/m^3 steps and two other mixes (M2 and M3) were designed (water contents of 165 and 145 l/ m^3, respectively). Previous work (Zhou, 2001; Menzies, 2002) has shown that some aspects of concrete performance can be affected detrimentally when the fines content is allowed to deplete with cement reduction. Therefore, it was considered important to investigate the effect of maintaining fines content (particles < 75 μm) of the concrete when cement and water contents were reduced. Thus, at each w/c ratio, two additional mixes, namely M2*f* and M3*f* with water contents equal to that of the Mixes M2 and M3, respectively, were designed with the fines contents equal to those of the corresponding Reference Mixes (M1s). This was achieved by inclusion of ground limestone powder as part of the sand content. The workability of all of these mixes was maintained at the Reference Mix (M1) level using a superplasticizing admixture, at an appropriate dosage, determined by trial mixing.

The effect of increasing the cement and water contents compared to the Reference Mix (M1) at fixed w/c ratio on concrete performance was also studied. For this work, a mix (M5) with increased water content (210 l/ m^3), giving higher workability (180 mm nominal slump), was developed at each w/c ratio. In addition, another mix (M4), at the same w/c ratio, having the same cement content as the Reference Mix (M1), but with increased workability (180 mm nominal slump) achieved using superplasticizing admixture, was also tested to examine the effect of increasing workability. Indeed, if there is no major difference between Reference Mix (M1) and Mix M4, the increase in workability associated with cement (and hence water) increase in Mix M5 compared to Reference Mix (M1), could be ignored. In both cases, the sand proportion in the mixes was increased compared to Reference Mix (M1) to maintain mix stability. The superplastizer dosage for the Mix M4 was determined by trial mixing.

Stage 2

Stage 2, which represented the major part of the study, was carried out to examine the effect of change in cement content at fixed w/c ratio on the resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion using small scale, uncracked specimens. In addition, permeation properties of concrete (which influence the transport of aggressive substances, oxygen and moisture in concrete, hence the corrosion activities) and resistance of concrete to carbonation, chloride diffusion and chloride ingress (which indicates the effectiveness of cover concrete, hence part of the whole corrosion process), were examined. As mentioned earlier, for this study, a range of cement and coarse aggregate combinations was used. PC, 42.5 N, the main cement type, was used with (i) natural gravel, (ii) granite and (iii) dolomitic magnesium limestone. The main coarse aggregate type, dolomitic magnesium limestone, was combined with (i) 100% PC, (ii) 70% PC / 30% PFA and (iii) 50% PC / 50% GGBS.

Figure 3.2 shows the experimental programme of work carried out in Stage 2. Following the guidelines given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), the w/c ratios 0.55 and 0.45 were used for concrete subjected to carbonation-and-chloride-induced reinforcement corrosion, respectively. Permeation properties, 28-day cube strength and some fresh properties were examined at both w/c ratios.

As for the Stage 1, a series of mixes was designed for each aggregate-cement combination at each w/c ratio to cover a range of cement contents. The water content required to achieve the Reference Mix (M1), *i.e.* a workability of 75 mm nominal slump without superplasticizing admixture, varied with aggregate and cement types between 175 and 190 l/m^3. The Reference Mix (M1), the cement-and-water-increased mix with 180 mm nominal slump (M5) and the cement-and-water-reduced (a 40 l/m^3 water reduction) mix with maintained fines content (M3*f*), were used for all aggregate-cement combinations. For the main aggregate-cement combination (dolomitic magnesium limestone and PC), two additional mixes, M2 (a 20 l/m^3 water reduction) and M2*f* (a 20 l/m^3 water reduction with fines content maintained) were considered to cover an intermediate cement content between Reference Mix (M1) and Mix M3*f*, and to examine the effect of cement reduction with-and-without maintained fines content.

Stage 3

In real-life, concrete structures can undergo cracking due to several causes. These cracks potentially allow corrosion to occur more rapidly than in uncracked concrete. Therefore, to examine this situation, Stage 3 was carried out to study the effect of variation in cement content at fixed w/c ratio on the resistance of cracked concrete to chloride penetration and chloride-induced reinforcement corrosion, using reinforced concrete beam specimens under static load conditions.

For this study, concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate was used. Following the requirements of BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), a w/c ratio of 0.45 was selected. At that w/c ratio, cement content was varied and Mixes M1 (Reference Mix), M5 and M3*f*, described in the earlier stages, were used. Given the significance of the crack width, three width sizes were used, namely 0.1, 0.3 and 0.5 mm. 0.1 mm is the boundary between microcracking and macrocracking (Neville, 1995; Li, 2000), while 0.3 mm is the maximum allowable crack width for reinforced concrete structures in aggressive environments, according to the guidelines given in BS 8110: Part 2 (BSI, 1985), and 0.5 mm provided a level beyond the allowable limit.

The experimental programme of stage 3 is outlined in Figure 3.3.

ROLE OF CEMENT CONTENT IN DETERMINING RESISTANCE OF CONCRETE TO REINFORCEMENT CORROSION

STAGE 1

MATERIALS

Cement: Portland Cement (PC), Grade 42.5 N
Filler: Limestone Filler
Sand: Natural Sand (Zone M of BS 882)
Coarse Aggregate: Dolomitic Magnesium Limestone (5 to 20 mm)
Admixture: Superplasticizer
Water: Mains Water (20°C)

MIX DETAILS
W/C RATIOS: 0.65, 0.55, 0.50, 0.45

Mix Reference	Nominal Slump, mm	Water Content[$], l/m^3
M5	180	210
M4[#]	180	185
M1	75	185
M2*f*[#]	75	165
M2[#]	75	165
M3*f*[#]	75	145
M3[#]	75	145

[$] *Cement content varied in equal proportion to maintain w/c ratio*
f *Filler included to maintain fines content equal to that of the Reference Mix (M1)*
[#] *Superplasticizer added to maintain workability*

CURING
Water, 20°C

PROPERTIES TESTED

FRESH
Workability (Slump)
Cohesion (Visual)
Finishability (Visual)
Plastic Density
Bleeding (W/C: 0.55*)
Air Content (W/C: 0.45)

ENGINEERING
Hardened Density
Cube Strength up to 180 Days
Flexural Strength
(W/C: 0.65, 0.55*, 0 .45*)
Modulus of Elasticity (W/C: 0.55)
Load to Failure (W/C: 0.55*)
Drying Shrinkage (W/C: 0.55)

PERMEATION AND DURABILITY
ISAT (W/C: 0.65, 0.55, 0 .45)
Air Permeability
(W/C: 0.65, 0.55, 0 .45)
Carbonation
(W/C: 0.65, 0.55*, 0.45*)
Chloride Diffusion - PD
(W/C: 0.65*, 0.55*, 0.45)
Sulfate Expansion (W/C: 0.45)
Freeze / Thaw (W/C: 0.45)
Abrasion Resistance (W/C: 0.50)

* *Selectively for number of mixes*

Figure 3.1 Outline of experimental programme of Stage 1

ROLE OF CEMENT CONTENT IN DETERMINING RESISTANCE OF CONCRETETO REINFORCEMENT CORROSION

STAGE 2

MATERIALS

CEMENTS

1. 100% PC, 42.5 N
2. 70% PC, 42.5 N and 30% PFA
3. 50% PC, 42.5 N and 50% GGBS

COARSE AGGREGATES

A. Crushed Granite (10 and 20 mm)
B. Natural Gravel (10 and 20 mm)
C. Dolomitic Magnesium Limestone (5 to 20 mm)

OTHER

Filler: Limestone Filler
Sand: Natural Sand (Zone M of BS 882)
Admixture: Superplasticizer
Water: Mains Water (20°C)
Reinforcement: High Yield Steel (f_y: 460 N/mm^2, 10 mm Dia.)

MIX DETAILS
W/C RATIOS: 0.55, 0.45

Mix Reference	Nominal Slump, mm	Water Content[$], l/m^3				
		Agg A/Cem 1	Agg B/Cem 1	Agg C/Cem 1	Agg C/Cem 2	Agg C/Cem 3
M5	180	215	195	210	200	210
M1	75	190	175	185	175	185
M2*f*[#]	75	---	---	165	---	---
M2[#]	75	---	---	165	---	---
M3*f*[#]	75	150	135	145	135	145

[$] *Cement content varied in equal proportion to maintain w/c ratio*
f *Filler included to maintain fines content equal to that of the Reference Mix (M1)*
[#] *Superplasticizer added to maintain workability*
--- Not Tested

CURING
(i) Water, 20°C (ii) Air, 55% RH, 20°C

PROPERTIES TESTED

FRESH
Workability (Slump)
Plastic Density

ENGINEERING
28-Day Cube Strength

PERMEATION
Capillary Porosity
Water Absorption
ISAT

DURABILITY
Carbonation (W/C: 0.55)
Chloride Diffusion – CD (W/C: 0.45)

REINFORCEMENT CORROSION
Carbonation-Induced (W/C: 0.55)
Chloride-Induced (W/C: 0.45)

Chloride Content (Total and Water-Soluble)
Corrosion Potential
Corrosion Current
Visual Inspection of Steel

Figure 3.2 Outline of experimental programme of Stage 2

ROLE OF CEMENT CONTENT IN DETERMINING RESISTANCE OF CONCRETETO REINFORCEMENT CORROSION

STAGE 3

MATERIALS

Cement: Portland Cement (PC), Grade 42.5 N
Filler: Limestone Filler
Sand: Natural Sand (Zone M of BS 882)
Coarse Aggregate: Dolomitic Magnesium Limestone (5 to 20mm)
Admixture: Superplasticizer
Water: Mains Water (20°C)
Reinforcement: High Yield Steel (f_y: 460 N/mm^2, 10 mm Dia.)

MIX DETAILS
W/C RATIO: 0.45

Mix Reference	Nominal Slump, mm	Water Content[$], l/m^3
M5	180	210
M1	75	185
M3*f*[#]	75	145

[$] *Cement content varied in equal proportion to maintain w/c ratio*
f *Filler included to maintain fines content equal to that of the Reference Mix (M1)*
[#] *Superplasticizer added to maintain workability*

CURING
Water, 20°C

TEST DETAILS
Specimen Size: 100 x 100 x 475 mm Beams
Cover to Reinforcement: 45 mm
Crack Width: 0.1*, 0.3 and 0.5* mm
Exposure: 6 Hours Wet / Dry to 3.5% NaCl Solution at 20 °C

PROPERTIES TESTED

REINFORCEMENT CORROSION
Chloride-Induced (W/C: 0.45)
Chloride Content (Water-Soluble)
Corrosion Potential
Corrosion Current
Visual Inspection of Steel

* *Selected for mix M5 only*

Figure 3.3 Outline of experimental programme of Stage 3

3.3 MATERIALS

3.3.1 Cement Types

Portland Cement (PC)

Portland cement of grade 42.5 N (normal early strength) used, conforming to BS 12 (BSI, 1996) and BS EN 197-1 (BSI, 2000). Its properties are given in Table 3.1. The cement was obtained from a single source and stored in air-and-watertight bags until use.

Pulverized-Fuel Ash (PFA)

The pulverized-fuel ash used, was from a single power station, conforming to BS 3892: Part 1 (BSI, 1997). Its properties are summarised in Table 3.1. The bulk supply was also stored in sealed bags until use. This material is classed as an addition, according to BS EN 197-1 (BSI, 2000). This means that it is not a cement on its own, but when added with PC at the concrete mixer or as a blended cement, the combination is considered as a cement.

Ground Granulated Blast-Furnace Slag (GGBS)

The ground granulated blast-furnace slag used, was from a single source, conforming to BS 6699 (BSI, 1992). Its properties are given in Table 3.1. Similar to other cements, it was stored in sealed bags until use. This material is also considered as an addition in the terminology of BS EN 197-1 (BSI, 2000).

3.3.2 Coarse Aggregate Types

Three normal weight aggregates were used, namely granite, natural gravel and dolomitic magnesium limestone, all conforming to BS 882 (BSI, 1992) and pr EN 12620 (CEN, 2000). Both natural gravel and granite were in two size fractions (5 to 10 mm and 10 to 20 mm). The dolomitic magnesium limestone was in a 5 to 20 mm all in size. Each material was obtained from a single bulk supply. These were laboratory dried at 20°C and 55% RH to constant mass prior to use, normally taking 24 hours. The main properties of coarse aggregates used in this study are given in Table 3.2. It can be noted that dolomitic magnesium limestone has a slightly higher aggregate impact value (AIV) and aggregate crushing value (ACV) compared to the other aggregates, indicating its lower resistance to pulverisation. In addition, its higher water absorption reflects higher porosity.

3.3.3 Natural Sand

Natural sand used in this study conformed to grading zone M (medium grade) of BS 882 (BSI, 1992). Table 3.3 summarises the main properties of the sand. Sand was laboratory dried for about 24 hours at 20°C and 55% RH to constant mass prior to use.

Table 3.1 Properties of cements

PROPERTY	PC, 42.5 N	PFA*	GGBS
Fineness, m^2/kg	405	7.2#	509
Loss-On-Ignition (LOI), %	1.4	5.0	0.9
Particle Density, Mg/m^3	3.14	2.27	2.90
Compressive Strength, N/mm^2			
1-day	19.5	--	--
2-day	31.5	--	--
7-day	45.5	--	--
28-day	60.0	--	--
Initial Setting Time, Minutes	115	--	--
Soundness, mm	0.0	--	--
Particle Size Distribution, % passing by volume			
125 µm		100	
100 µm	100	99.9	100
75 µm	99.9	98.6	99.9
45 µm	96.7	91.9	95.1
25 µm	79.4	79.0	80.1
10 µm	40.3	53.7	50.0
5 µm	22.5	34.7	33.3
2 µm	10.5	16.8	17.3
1 µm	5.1	7.1	7.6
0.7 µm	1.2	2.7	3.0
0.5 µm	0.3	0.2	0.3
0.1 µm	0	0	0
Bulk Oxide Composition, %			
SiO_2	21.0	46.9	35.8
Al_2O_3	4.9	23.2	13.7
Fe_2O_3	2.6	8.8	0.5
CaO	64.6	3.4	41.0
MgO	1.2	0.8	5.9
P_2O_5		0.05	0.04
TiO_2		1.5	0.4
SO_3	3.3	2.3	1.0
K_2O	0.7	3.7	0.3
Na_2O	0.1	4.4	0.2
MnO		0.09	0.17
Bogue Composition, %			
C_3S	53.0	--	--
C_2S	21.0	--	--
C_3A	8.5	--	--
C_4AF	8.0	--	--

** Water demand = 96%; Strength factor = 0.88*

 # % retention on 45µm sieve

-- Not applicable

Table 3.2 Properties of coarse aggregates

PROPERTY	NATURAL GRAVEL		GRANITE		DOLOMITIC MAGNESIUM LIMESTONE
	5-10 mm	10-20 mm	5-10 mm	10-20 mm	5-20 mm
Shape, Visual	Rounded		Angular		Angular
Surface Texture, Visual	Smooth		Coarse crystalline		Rough
Flakiness Index*, %	11		12		9
Elongation Index*, %	14		29		17
Aggregate Impact Value#, %	24		25		34
Aggregate Crushing Value#, %	20		20		28
Water Absorption (Laboratory dry to SSD), %	1.3	1.2	0.6	0.5	3.8
Particle Density (SSD), Mg/m^3	2.59	2.60	2.62	2.63	2.60
Bulk Density (SSD), Mg/m^3					
Loose	1.59	1.55	1.33	1.37	1.30
Compacted	1.66	1.65	1.49	1.49	1.42
Grading, % passing by mass					
37.5 mm		100		100	100
20 mm		96		85	99
14 mm	100	74	100	13	69
10 mm	91	24	92	2	30
6.3 mm	46		25	1	
5 mm	18	4	13		6
2.36 mm	4		2		
0.075 mm	0	0	0.3	0.1	3.0
Bulk Oxide Composition, %					
SiO_2	65.4	66.1	72.3	70.2	1.0
Al_2O_3	11.7	12.6	14.8	15.7	0.5
Fe_2O_3	10.0	5.6	3.6	2.1	1.1
CaO	2.7	4.2	1.6	1.3	37.2
MgO	1.4	2.0	0.3	0.2	13.2
P_2O_5	0	0	0.1	0	0
TiO_2	0.7	0.7	0.3	0.3	0
SO_3	0.1	0.1	0.1	0.1	0.1
K_2O	1.7	1.9	1.9	5.3	0.1
Na_2O	2.8	2.9	3.8	3.7	0.2
MnO	0.1	0.1	0.1	0.1	0
Loss-On-Ignition (LOI), %	3.4	3.8	1.0	1.0	46.6
Chloride Content, %	<0.01	<0.01	<0.01	<0.01	<0.01

** 6.3 mm to 20 mm sample*

 # 10 mm to 20 mm sample

Table 3.3 Properties of natural sand

PROPERTY	VALUE
Water Absorption (Laboratory dry to SSD), %	0.5
Particle Density (SSD), Mg/m^3	2.63
Bulk Density (SSD), Mg/m^3	
Loose	1.58
Compacted	1.68
Grading, % passing by mass	
5 mm	100
2.36 mm	96
1.18 mm	90
0.60 mm	77
0.30 mm	43
0.15 mm	8
0.075 mm	1
Bulk Oxide Composition, %	
SiO_2	78.5
Al_2O_3	10.5
Fe_2O_3	3.0
CaO	1.5
MgO	0.9
P_2O_5	0.1
TiO_2	0.5
SO_3	0.1
K_2O	1.6
Na_2O	2.0
MnO	0.1
Loss-On-Ignition (LOI), %	1.2
Chloride Content, %	<0.01

3.3.4 Other Materials

Limestone Powder (Filler)

A ground limestone powder, conforming to BS 7979 (BSI, 2001), was used as a filler in some concrete mixes to maintain the fines content (particles < 75 μm). The limestone powder was a very fine material (about four times finer than PC) and is considered chemically inert in the presence of water. As with the other materials, this was also obtained from a single source and stored in air-and-watertight bags prior to use. The properties of the material are given in Table 3.4.

Table 3.4 Properties of limestone powder

PROPERTY	VALUE
Fineness, m^2/kg	1600
Loss-On-Ignition (LOI), %	43.6
Oil Absorption, ml/100g	19.0
Particle Density, Mg/m^3	2.65
Bulk Density (SSD), Mg/m^3	
Loose	0.83
Compacted	1.05
Particle Size Distribution, % passing by volume	
100 µm	100
75 µm	99.6
45 µm	98.4
25 µm	92.9
10 µm	65.0
5 µm	37.6
Bulk Oxide Composition, %	
SiO_2	0.00
Al_2O_3	0.06
Fe_2O_3	0.02
Calcium as CaO	55.46
Calcium as $CaCO_3$	99.04
MgO	0.24

Superplasticizing Admixture (SP)

A superplasticizing admixture, conforming to BS EN 934: Part 2 (BSI, 2001), was used to control the workability of some concrete mixes. Its chemical structure consists of a carboxylic ether polymer with long side chains, which causes dispersion of cement particles, thereby allowing reductions in water contents whilst maintaining a workable concrete. The SP was a dark brown coloured liquid with a specific gravity of 1.10 at 20°C and no chlorides present.

Water

In accordance with BS 3148 (BSI, 1980), mains water at 20°C was used for concrete mixes, curing and the majority of tests, unless indicated otherwise.

Steel Reinforcement

Hot rolled, deformed, type 2 steel reinforcement bars of 10 mm diameter and 460 N/mm^2 grade, conforming to BS 4449 (BSI, 1997), were used.

Sodium Chloride

Analytical reagent grade sodium chloride (99.8% NaCl) was used in the chloride diffusion and exposure solutions for the corrosion tests.

3.4 MIX DESIGN AND MIX PROPORTIONS

Concrete mixes were designed using the method published by the Building Research Establishment (Teychenne *et al*, 1997). In the mix design process, w/c ratio, water content and workability (slump) were considered as the starting parameters. As mentioned in Section 3.2, workability was controlled through the water content (Mixes M1 and M5) or the addition of superplasticizing admixture (Mixes M2*f*, M2, M3*f*, M3 and M4). Corresponding cement contents were obtained by calculation (dividing the water content by the w/c ratio). Then, referring to Figure 5 of the BRE document, the wet density of concrete was estimated using the relative density of the combined aggregate at saturated surface dry condition (fine and coarse) and the water content. This allowed calculation of the total aggregate content (by subtracting the cement and water contents from the wet density). As the next step, the proportion of sand (as a percentage of the total aggregate content) was determined, based on the maximum coarse aggregate size, nominal slump, w/c ratio and sand grading (Figure 6 of the BRE method). Finally, the sand content (multiplying the total aggregate content by the sand proportion) and coarse aggregate content (subtracting the calculated sand content from the total aggregate content) were determined.

For mixes containing PFA and GGBS, calculations were carried out assuming 100% PC and, then, PFA or GGBS was included at the required level by mass. To maintain the yield of the concrete mix, the sand content was adjusted appropriately, as the relative densities of the additions were different to that of PC. Due to the water reducing qualities of PFA, a 10 l/m^3 water reduction was possible compared to PC concrete whilst maintaining the same workability.

After determining the initial mix proportions, a correction for concrete yield was applied to all mix constituents, based on their particle densities (saturated surface dry density for aggregates) and plastic density measurements during trial mixing, thereby ensuring the mix proportions gave 1 m^3 of concrete.

To illustrate the mix design process, calculations for Mixes M1, M2 and M2*f* at fixed w/c ratio 0.55 for concrete made with PC, dolomitic magnesium limestone coarse aggregate and natural sand, are given in Appendix B.

It should be noted that the mix design process gives the aggregate quantities at saturated surface dry condition. Therefore, when they were batched at laboratory dry condition, lower masses were

used with additional water, to allow for water absorption by aggregates from the laboratory dry to saturated surface dry conditions. The Plastic density of concrete was used as a check on the mix design and batching procedures.

Tables 3.5 (a) to (e) give the mix proportions for all the concrete used in this project, together with their measured plastic densities.

Table 3.5 (a) Concrete mix proportions and plastic densities

Natural gravel coarse aggregate and 100% PC, 42.5 N cement

W/C Ratio	Mix	PC	Filler	Total Fines	SP, % fines	Free Water	Natural Sand	Natural Gravel		Sum of Mix Constituents	Plastic Density
								5-10 mm	10-20 mm		
0.55	M5*	355	0	361	0	195	630	390	781	2351	2360
	M1	320	0	326	0	175	564	439	879	2377	2390
	M3*f*[#]	245	75	325	0.40	135	539	480	954	2428	2430
0.45	M5*	438	0	444	0	196	573	387	769	2363	2375
	M1	391	0	396	0	176	512	436	873	2388	2415
	M3*f*[#]	301	90	396	0.30	135	471	481	958	2436	2445

All units kg/m^3, except water content l/m^3
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Table 3.5 (b) Concrete mix proportions and plastic densities

Granite coarse aggregate and 100% PC, 42.5 N cement

W/C Ratio	Mix	PC	Filler	Total Fines	SP, % fines	Free Water	Natural Sand	Granite		Sum of Mix Constituents	Plastic Density
								5-10 mm	10-20 mm		
0.55	M5*	391	0	397	0	215	614	374	747	2341	2355
	M1	345	0	351	0	190	561	426	851	2373	2385
	M3*f*[#]	273	72	350	0.40	150	539	464	928	2426	2435
0.45	M5*	478	0	484	0	215	556	369	737	2355	2370
	M1	422	0	427	0	190	513	420	840	2385	2400
	M3*f*[#]	333	89	427	0.39	150	476	463	925	2436	2460

All units kg/m^3, except water content l/m^3
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Table 3.5 (c) Concrete mix proportions and plastic densities

Dolomitic magnesium limestone coarse aggregate and 100% PC, 42.5 N cement

W/C Ratio	Mix	PC	Filler	Total Fines	SP, % fines	Free Water	Natural Sand	Limestone 5-20 mm	Sum of Mix Constituents	Plastic Density
	M5*	323	0	330	0	209	666	1128	2326	2320
	M4*#	283	0	290	0.25	184	701	1193	2361	2370
	M1	283	0	289	0	184	606	1287	2360	2360
0.65	M2*f*#	254	30	290	0.29	164	603	1340	2391	2385
	M2#	254	0	260	0.34	164	632	1340	2390	2385
	M3*f*#	224	60	290	0.45	144	597	1388	2413	2405
	M3#	224	0	231	0.52	144	657	1388	2413	2390
	M5*	379	0	385	0	210	614	1133	2336	2335
	M4*#	334	0	340	0.24	185	649	1203	2371	2370
	M1	334	0	339	0	184	548	1301	2367	2370
0.55	M2*f*#	299	35	339	0.28	165	544	1352	2395	2390
	M2#	299	0	305	0.33	165	579	1352	2395	2395
	M3*f*#	265	70	340	0.44	145	535	1410	2425	2425
	M3#	265	0	271	0.50	145	604	1409	2423	2420
	M5*	420	0	426	0	210	580	1130	2340	2360
	M4*#	370	0	376	0.24	185	619	1199	2373	2375
	M1	370	0	375	0	185	529	1289	2373	2385
0.50	M2*f*#	330	40	375	0.26	165	510	1355	2400	2400
	M2#	330	0	336	0.32	165	550	1355	2400	2405
	M3*f*#	290	80	375	0.43	145	495	1416	2426	2425
	M3#	290	0	296	0.49	145	575	1415	2425	2430
	M5*	467	0	473	0	211	552	1119	2349	2340
	M4*#	411	0	417	0.27	185	586	1197	2379	2380
	M1	411	0	416	0	185	501	1283	2380	2380
0.45	M2*f*#	366	45	416	0.29	165	481	1348	2405	2410
	M2#	366	0	371	0.37	165	526	1348	2405	2395
	M3*f*#	321	90	416	0.49	145	461	1413	2430	2435
	M3#	321	0	327	0.53	145	551	1413	2430	2410

All units kg/m^3, except water content l/m^3
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Table 3.5 (d) Concrete mix proportions and plastic densities

Dolomitic magnesium limestone coarse aggregate and 70% PC, 42.5 N / 30% PFA

W/C Ratio	Mix	PC	PFA	Filler	Total Fines	SP, % fines	Free Water	Natural Sand	Limestone 5-20 mm	Sum of Mix Constituents	Plastic Density
0.55	M5*	255	109	0	370	0	199	594	1161	2318	2310
	M1	223	96	0	324	0	174	539	1320	2352	2330
	M3*f*[#]	172	73	75	325	0.48	135	519	1436	2410	2380
0.45	M5*	312	133	0	451	0	200	552	1152	2349	2325
	M1	273	117	0	395	0	175	472	1317	2354	2335
	M3*f*[#]	210	90	90	394	0.52	135	441	1445	2411	2385

All units kg/m^3, except water content l/m^3
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Table 3.5 (e) Concrete mix proportions and plastic densities

Dolomitic magnesium limestone coarse aggregate and 50% PC, 42.5 N / 50% GGBS

W/C Ratio	Mix	PC	GGBS	Filler	Total Fines	SP, % fines	Free Water	Natural Sand	Limestone 5-20 mm	Sum of Mix Constituents	Plastic Density
0.55	M5*	190	190	0	386	0	210	599	1132	2321	2315
	M1	167	167	0	339	0	184	536	1304	2358	2325
	M3*f*[#]	133	133	75	346	0.30	145	524	1410	2420	2395
0.45	M5*	234	234	0	473	0	211	534	1119	2332	2310
	M1	206	206	0	417	0	185	485	1284	2366	2340
	M3*f*[#]	161	161	90	417	0.42	145	450	1413	2420	2390

All units kg/m^3, except water content l/m^3
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

3.5 CONCRETE SPECIMEN PREPARATION

3.5.1 Batching of Materials

Cements, aggregates (at laboratory dry condition) and water were batched by mass to an accuracy of ± 0.005 kg. The superplasticizing admixture was batched by mass to an accuracy of ± 0.1 g.

3.5.2 Concrete Mixing

Mixing of concrete was carried out following the procedures described in BS 1881: Part 125 (BSI, 1986), using a horizontal pan mixer of 0.04 m^3 capacity. Firstly, aggregates were placed in the pan and mixed for 30 seconds. Then, approximately half of the mix water was added and mixing continued for 1 minute. After thorough hand mixing, 8 minutes were allowed for aggregates to absorb water (pan covered). All cements and limestone filler (if used) were mixed thoroughly and added to the mixer. Mixing was continued for another 1 minute. After hand mixing to ensure homogeneity of the mix, the remaining mix water (including superplasticizing admixture, where used, stirred to ensure effective dispersion) was added and mixing carried out for a further minute. Finally, after a brief hand mix, mixing was continued for another $1^1/_2$ minutes.

3.5.3 Specimen Casting

After testing for fresh properties, concrete was cast immediately into steel moulds coated with oil, following the procedures described in BS 1881: Part 108, 109 and 110 (BSI, 1983), in terms of size tolerances and method of casting. Filling and vibration were done in two layers for moulds with vertical dimension less than 100 mm and three layers for others. The vibration process, which normally took about 15 seconds, was carried out using a vibrating table. After the final layer was compacted, the top surface was finished and smoothened using a float.

3.5.4 Specimen Curing

The filled moulds were stored at 20°C for 24 hours under a tentage of damp hessian and polythene sheeting to maintain high humidity (> 95% RH) prior to demoulding. After demoulding, specimens were water (20°C) or air (20°C and 55% RH) cured as appropriate until testing. The water curing procedure followed the guidelines given in BS 1881: Part 111 (BSI, 1983).

3.6 TEST TECHNIQUES AND PROCEDURES

3.6.1 Fresh Properties

Workability

Workability of concrete was measured using the slump test described in BS EN 12350: Part 2 (BSI, 2000).

Plastic Density

Plastic density of fresh concrete was calculated from the mass of fully compacted (five approximately equal layers) concrete in a container of 200 mm diameter and 300 mm height, as described in BS 1881: Part 107 (BSI, 1983).

Cohesion

Immediately after measuring workability, a visual assessment was made on the same concrete (slumped concrete) following the guidelines given in Note 1, Clause 6 of BS 1881: Part 102 (BSI, 1983). For this study, the side of the slumped concrete was gently tapped five times with the slump test's compacting rod, thus, causing it to slump further. The cohesion of concrete was defined by five classes, as given in Table 3.6.

Finishability

As there is no standard test method to determine the finishability of concrete, it was assessed visually. For this, a float was passed over the concrete surface ten times with an even pressure. The resultant surface finish was assessed visually within the classification scheme given in Table 3.7.

Table 3.6 Classification of cohesion property for fresh concrete

CLASS	COHESION PROPERTY	
	Description	**Observation***
1	Over cohesive	Little further slump
2a	Very cohesive	Gradually slumps further, no shearing
2b	Cohesive	Gradually slumps further, some shearing
2c	Little cohesion	Gradually slumps further then, partial collapse
3	No cohesion	Slumped concrete shears

** Behaviour of slumped concrete after gentle tapping*

Table 3.7 Classification of finishability characteristics for fresh concrete

CLASS	FINISHABILITY CHARACTERISTICS	
	Description	**Observation***
1	Very good finishability - little effort required to finish	Smooth surface, few voids
2	Good finishability - moderate effort required to finish	Smooth surface, some voids
3	Unacceptable finishability - difficult to finish	Uneven surface, exposed aggregate

** Appearance of concrete surface after ten passes with float*

Air Content

The air content of fresh concrete was measured using a Capco direct reading air content meter, following Method B described in BS 1881: Part 106 (BSI, 1983). The 8 litre capacity steel

container was filled with concrete in three equal layers, compacting each layer with 25 strokes of a 25 mm square cross sectional, 380 mm long rod. After compaction of each layer, the sides of the container were struck with a mallet to remove entrapped air. The lid was clamped in place and water was poured on top of the concrete to replace the air gap between the lid of the container and the concrete. A known pressure was applied and, on releasing, the apparent air content was measured. An aggregate correction factor was determined for a combined sample of coarse and fine aggregates, as described in the Standard and subtracted from the apparent air content to obtain the true air content.

Bleeding

Bleeding of fresh concrete was monitored in accordance with Method A (sample consolidated by tamping) given in ASTM C232 (ASTM, 1999). The concrete was placed into a weighed steel cylindrical container of approximately 14 litre capacity in two equal layers, leaving about 30 mm at the top edge of the container. Each layer was compacted with 50 strokes of a tamping rod, after which the outside of the container was struck several times with a mallet to remove air voids. After the second layer, the concrete surface was smoothed by trowelling. The container with concrete was weighed and, then, covered to prevent evaporation of bleed water. After 10, 20, 30, 60 and 120 minutes, the container was tilted slightly for 60 seconds and the accumulated bleed water was collected with a disposable plastic pipette and weighed. At each time, the cumulative bleed water was expressed as a percentage of the free mix water contained within the test specimen.

3.6.2 Engineering Properties

Compressive Strength

Compressive strength of hardened concrete was measured in accordance with BS 1881: Part 116 (BSI, 1983), using 100 mm cubes. At each test age, two or three water-cured (20°C) cubes were loaded at a rate of 18 N/mm^2 per minute until failure.

Flexural Strength

Flexural strength tests were carried out in accordance with BS 1881: Part 118 (BSI, 1983), using two 100 x 100 x 500 mm prism specimens water-cured at 20°C to the age of 28 days. The specimens were loaded at third points at a rate of 3.6 N/mm^2 per minute until failure in flexure.

Static Modulus of Elasticity

The static modulus of elasticity of concrete in compression was obtained in accordance with BS 1881: Part 121 (BSI, 1983), using the mean of two cylinders of 150 mm diameter x 300 mm height, at the age of 28 days (water-cured at 20°C). Immediately prior to testing, the top surface of the cylinder specimens was capped using a molten sulphur / sand compound to ensure a flat, even

surface for loading. The modulus of elasticity was calculated from the stress / strain relationship obtained on loading the specimen to 0.33 $f_{cu,28}$, where $f_{cu,28}$ is the mean 28-day compressive strength of 100 mm cubes.

Load to Failure

Cylinders, of similar size to those used for the modulus of elasticity test, were used (one specimen water-cured at 20°C to the age of 28 days) to determine the stress / strain characteristics of concrete on loading to failure. The method developed by Munday (1977) was used which allowed a constant strain rate to be applied such that after the maximum load, the testing machine adjusted its load in response to the resistance of the failing concrete. To achieve this, a compression testing machine set at a constant rate of strain (0.0005 per minute) was used. Every 15 seconds during the test, the applied load was noted and the axial deformation measured using two dial gauges set on the opposite sides of the specimen.

Drying Shrinkage

Drying shrinkage of concrete was monitored using two prism specimens of 75 x 75 x 300 mm with stainless steel studs cast at both ends to allow accurate measurement of their axial length. After 7 days of water-curing (20°C), axial lengths of the specimens were measured using a dial gauge attached to a steel frame to an accuracy of ± 0.002 mm. Thereafter, the prisms were stored in a drying room at 20°C and 55% RH and the lengths re-measured after 1, 2, 4, 6, 8, 12, 16 and 20 weeks of storage. The length reduction after a given drying time (taken as the mean of the two specimens) was expressed as a proportion of the original length.

3.6.3 Permeation Properties

Capillary Porosity

Capillary porosity tests were carried out in accordance with the method given in BS 1881: Part 124 (BSI, 1988), using two cores of 54 mm diameter x nominally 50 mm long, cut from a 100 mm cube at the age of 28 days (water-cured at 20°C). The specimens were oven-dried at 105°C to constant mass (< 0.1% change in weight over 24 hours), which typically took 48 hours and cooled in a desiccator prior to testing. The dry specimens were weighed, fully immersed in toluene solution and placed in a vacuum desiccator. The vessel's pressure was reduced to less than 13.5 kPa and the specimens were left for 24 hours to allow removal of capillary air. The pressure was, then, released and a sharp tap was given to the vessel to remove all entrapped air. The samples were kept immersed in the solution at atmospheric pressure for a further 5 minutes. Thereafter, the samples were quickly removed and excess solution was wiped from the concrete surface before measuring the wet weights of the samples using pre-weighed sealable polyethylene bags. The equivalent mass of water required to fill the pores was found using the difference between wet and dry weights of

the sample and the relative density of the toluene solution. The equivalent mass of water required to fill the pores was given as a percentage of the dry mass of the sample to express the capillary porosity.

Water Absorption

The water absorption test was carried out using 28-day water-cured (20°C), 100 mm cube specimens. These were oven-dried and cooled as for the capillary porosity test prior to testing. One specimen was used for each concrete mix. After measuring the initial weights, the cubes were partially immersed in water at 20°C to a depth of 25 mm. At time intervals of $^1/_2$, 1 and 24 hours, the specimens were removed from the water and weights were recorded after wiping excess water from the concrete surface. The weight increase as a percentage of the initial weight was used to express the water absorption at a given time period.

Initial Surface Absorption (ISA)

The initial surface absorption test was carried out in accordance with the method described in BS 1881: Part 208 (BSI, 1996), using 28-day water-cured (20°C), 150 mm cube specimens. Prior to testing, the specimens were oven-dried at 105°C to constant mass, usually taking about 2 weeks and, then, cooled in a desiccator. The test apparatus consisted of a perspex cap with an area of 5000 mm^2, connected to a horizontal, calibrated capillary tube and a 200 mm head of water via flexible tubes. To start the test, the cap was clamped onto the concrete surface and water was allowed to move into the cap by opening the valve attached to the water reservoir and exit the equipment via the capillary tube. Once water touched the concrete surface, time measurement was started using a clock. After 10, 30 and 60 minutes, the valve attached to the water reservoir was temporarily closed and the water movement along the capillary tube during 1 minute was recorded. The measured distance was multiplied by the calibration factor of the apparatus to determine the absorption. For each mix, one specimen was used and the mean of readings from two opposite sides (avoiding the top and bottom surfaces of the cube, as cast) taken as the initial surface absorption.

Air Permeability

Air permeability of concrete was measured in accordance with a method developed at the University of Dundee (Dhir *et al*, 1989), using a triaxial compression cell as the testing apparatus. The test measures air outflow rates for a range of inlet pressures, allowing intrinsic permeability (k in m^2) to be calculated. As for the capillary porosity test, two oven-dried and cooled core specimens cut from a 100 mm cube at the age of 28 days (water-cured at 20°C) were used. After the specimen (cylindrical side pre-coated with grease) was properly clamped in the compression cell, a constant circumferential air pressure was applied and maintained throughout the test to

achieve an air-tight seal between the specimen and the cell. Then, the inlet air pressure was applied, starting from 110 psi (0.76 N/mm²) and reducing in steps of 20 psi (0.14 N/mm²) until either 30 psi (0.21 N/mm²) was reached or the outflow rate was less than 6 cc/min. For each inlet pressure, the outflow rate reading was taken after steady-flow conditions were achieved, which typically took about 5 minutes. The intrinsic air permeability was calculated using the solution to Darcy's law, proposed by Dhir *et al* (1989). This assumes that for each inlet air pressure, there is an apparent intrinsic air permeability (k' in m²), which is calculated from

$$k' = 2\mu LP_2Q_2 / A(P_1^2 - P_2^2)$$

where, μ = viscosity of air at 20°C (1.79×10^{-5} kg/ms)

L = measured length of the specimen (m)

P_1 = sum of inlet air pressure and atmospheric pressure (N/m^2)

P_2 = outlet pressure / atmospheric pressure (101,000 N/m^2)

A = cross sectional area of the specimen (m^2)

Q_2 = outflow rate (m^3/s).

The apparent intrinsic air permeability for each inlet air pressure was plotted against $1/P_m$, where P_m is the average pressure within the specimen (average of P_1 and P_2). The resulting, approximately straight line was extrapolated to determine the intrinsic air permeability at infinite mean pressure.

3.6.4 Durability Properties

Carbonation Resistance

The carbonation rate was determined using prism specimens of 100 x 100 x 500 mm in accordance with a method developed by Dhir *et al* (1985). An accelerated carbonation exposure was used at carbon dioxide (CO_2) concentration of 4%, temperature of 20°C and relative humidity of 55%. After curing to 28 days (water-curing at 20°C or air-curing at 20°C and 55% RH), the specimens were dried in air at 20°C and 55% RH for 14 days. Prior to accelerated exposure (for up to 20 or 24 weeks), the specimens were wax-sealed on five faces (*i.e.* leaving exposed one longitudinal face that was vertical at casting) to ensure CO_2 ingress through only one surface. The test specimens were periodically removed from the CO_2 chamber and two approximately 50 mm thick slices were obtained from both ends by inducing a tensile fracture. The freshly exposed concrete surfaces were sprayed with phenolphthalein indicator solution (1 g of phenolphthalein, 70 ml of industrial alcohol and 30 ml of distilled, de-ionised water) to allow measurement of carbonation depth. The solution turned uncarbonated concrete pink (pH > 9), whereas that which had carbonated was colourless (pH < 9). From each slice, five carbonation depths were measured perpendicular to the exposed surface within the central portion to avoid any corner effects. If a large aggregate was split at a measuring location, the two readings on either side of the aggregate were averaged. The average

carbonation depth was found using ten readings (five readings from each slice). Following measurements, the ends of the prisms were resealed with wax and returned to the CO_2 chamber.

Chloride Diffusion

The chloride diffusion coefficient was determined in accordance with procedures developed at the University of Dundee (Dhir *et al*, 1990 a), using two test methods, namely the potential difference (PD) test and concentration difference (CD) test. The PD test is a rapid test method, which accelerates the passage of chloride ions through concrete by application of an electrical potential difference. In the CD test, chloride ions diffuse naturally through concrete due to a concentration difference. Two slices (100 mm diameter x 25 mm thick) were tested for each mix, the slices being cut at the age of 28 days (water-cured at 20°C), from the upper end (at casting) of a 100 mm diameter and 300 mm long cylinder, discarding the top 10 mm to avoid the variability associated with concrete near surfaces. The slices were circumferentially sealed near the base of the two-compartment plastic test cells using silicon. Both sides of the specimens (sealed in the diffusion cells) were fully water saturated prior to use for the PD or the CD test to prevent fast absorption of chloride ions. Immediately before starting the tests, the reservoir of each cell was filled with 750 ml of distilled, de-ionised water (saturated with calcium hydroxide only for the CD test).

The experimental arrangement of the PD test is shown in Figure 3.4. The diffusion cells were partially immersed in 5 molar (M) sodium chloride solution (177,250 ppm chloride ion concentration). A thin stainless steel plate was fully immersed in the sodium chloride solution to act as the cathode and a graphite rod was inserted into the distilled, de-ionised water through the top opening of each cell as an anode. A potential difference of 7.5 V was applied across the test specimens using a DC power supply. The build-up chloride ion concentration in the cells was measured using an ion-selective electrode (ISE) on a daily basis until the achievement of steady state conditions (typically in about 10 to 14 days). In order to determine the chloride diffusion coefficient, Fick's first law of diffusion was applied, as suggested by Dhir *et al* (1990 a). From the gradient of the steady state section of the graph of chloride ion concentration against time, the diffusion coefficient (D in cm^2/s) was calculated using the following formula.

$$D = mVL / A$$

where, m = rate of increase in chloride ion concentration in the cell (ppm/s)

V = volume of water in the cell (cm^3)

L = thickness of the slice (cm)

A = exposed area of the slice (cm^2).

The CD test procedure was very similar to the PD test except that there no electrodes were used. The chloride ion concentration in the cells was measured using the ISE monthly until reaching

steady state conditions (typically required 12 to 18 months), and the same procedure was used to calculate the diffusion coefficient. For concrete containing GGBS, a small sample was taken from the cell (monthly) and chloride concentration was found using a potentiometric titration method with silver nitrate, as the GGBS could release sulfides that may damage the ISE.

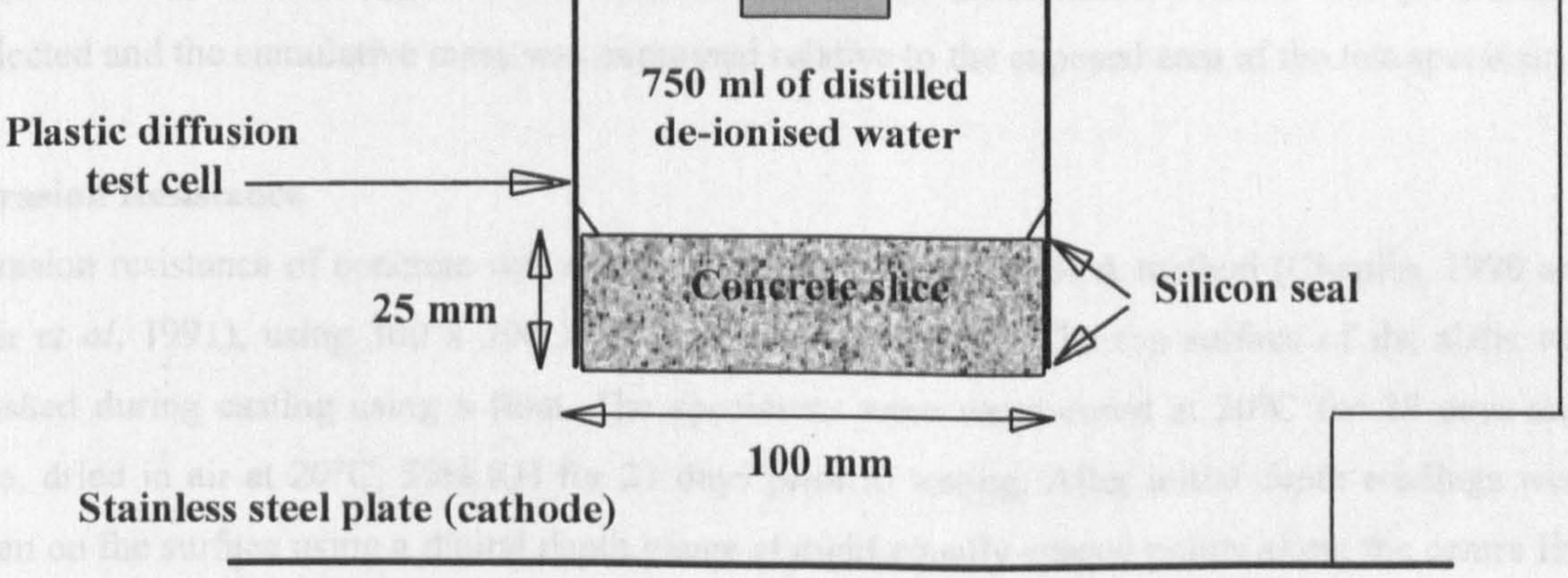


Figure 3.4 Experimental arrangement of chloride diffusion test (PD)

Sulfate Resistance

Sulfate expansion was monitored using two 75 x 75 x 300 mm prisms cast with stainless steel studs at both ends, as used for the drying shrinkage test. The prisms were water-cured (20°C) for 28 days and immersed in a 5% sodium sulfate ($Na_2SO_4 .10H_2O$) solution at 20°C. Axial expansion was measured at regular intervals, as for the drying shrinkage test, and was expressed as a proportion of the initial length (from the mean of the two specimens). The exposure condition used, was approximately 5.6 times stronger than the most severe environment (class 5: 6 g/l of sulfates) defined in BRE Digest 363 (BRE, 1996).

Freeze / Thaw Resistance

Freeze / thaw resistance of concrete was assessed in accordance with the proposed draft, pr EN/TC 51 slab scaling test (CEN, 1994), using two 150 x 150 x 50 mm specimens cut from a 150 mm cube. The cubes were water-cured (20°C) for 7 days and, then, air-cured (20°C, 55% RH) for a further 14 days prior to cutting into slabs. The cutting was done perpendicular to the top surface of the cubes at casting and the innermost concrete became the test face of the slabs. After drying in air for a further 5 days, rubber sheeting was glued with a contact adhesive on the base and sides of the slab, up to 20 mm above the test face, thus, enabling the creation of a reservoir on top of the slab. The joints between the test surface and the rubber sheeting were sealed using silicon to prevent leakage of the freezing medium. After the silicon hardened, water was poured onto the test face and the ponded specimen left for 5 days to achieve complete saturation. At the age of 31 days, water in the reservoir was replaced by 67 ml of freezing medium (3% sodium chloride solution) and the specimens were exposed to 56 freeze / thaw cycles with the temperature ranging from +20°C to -20°C over the 24 hour cycle period. During the test, the sides and base of the slabs were protected by polystyrene insulation and the top was covered with a plastic sheet to minimise evaporation of the freezing medium. Scaled material on the concrete surface was periodically collected and the cumulative mass was expressed relative to the exposed area of the test specimen.

Abrasion Resistance

Abrasion resistance of concrete was examined using a modified BCA method (Chaplin, 1990 and Dhir *et al*, 1991), using 300 x 300 x 100 mm slab specimens. The top surface of the slabs was finished during casting using a float. The specimens were water-cured at 20°C for 28 days and, then, dried in air at 20°C, 55% RH for 21 days prior to testing. After initial depth readings were taken on the surface using a digital depth gauge at eight equally spaced points along the centre line of the abrasion track, the slab was firmly fixed in position in the abrasion machine and levelled. The surface of the concrete specimen was abraded for 15 minutes through sliding, scraping and percussion actions by wheels rotating in a circular path. Thereafter, depths were re-measured at the original points and the abrasion depth was calculated from the depth difference. The abrasion depth was expressed as the average of eight readings taken at each of the eight points.

3.6.5 Resistance to Reinforcement Corrosion

Carbonation-Induced Corrosion

Resistance of concrete to carbonation-induced reinforcement corrosion was examined using two 100 mm cube specimens, following test procedures developed at the University of Dundee (Dhir *et al*, 1992), with a 10 mm diameter steel bar located to give 25 mm of cover. The steel bars were cut into approximately 120 mm lengths and grit blasted to ensure all steel was in a similar condition prior to testing. A small hole (3.4 mm diameter x 12 mm deep) was drilled into one end

of each bar to connect a copper wire using a self-tapping screw to allow electrical connection for subsequent corrosion analysis. Then, ends of the steel bars were sealed with two coats of anti-corrosive pitch epoxy resin to avoid end corrosion, leaving a 60 mm exposed length (18.9 cm^2 exposed area) at the centre. Prior to casting, the working and counter electrodes (the test and secondary bars) were placed in a pre-drilled steel mould at 25 mm from the top and the bottom, respectively. The bars were secured using silicon to avoid movement during compaction. After demoulding, the protruding bars were coated with pitch epoxy resin and the specimens were air-cured to accelerate subsequent carbonation (20°C and 55% RH) for 28 days, together with 100 mm sacrificial plain concrete cubes, which were required to determine the carbonation depth. Thereafter, all the faces of the specimens except the test faces were coated with two coats of silane primer and sealed with paraffin wax, thereby enabling carbonation to occur through one surface only. The specimens were exposed to the 4% CO_2 environment at 20°C and 55% RH. When the specimens were carbonated to a depth of 35 mm (full depth of the test bar), they were transferred to a high humid environment (20°C, 95% RH) to induce reinforcement corrosion (up to 24 weeks). Monitoring of corrosion initiation and propagation was made using corrosion potential and polarisation resistance measurements immediately prior to, and at different ages during the post-carbonation exposure. After 24 weeks, the cubes were split and the steel recovered for visual examination. A schematic cross section of a reinforced concrete specimen is shown in Figure 3.5.

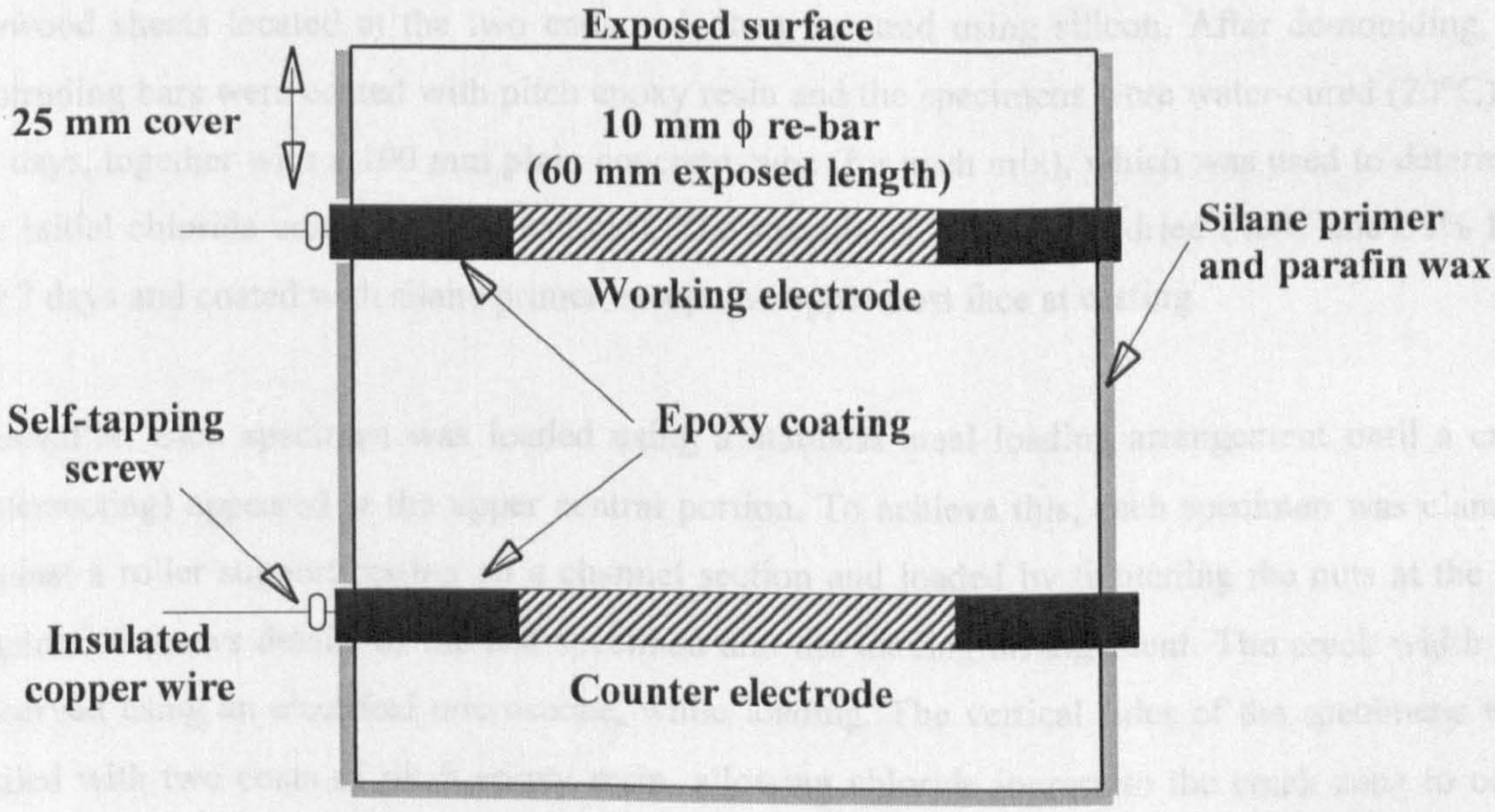


Figure 3.5 Schematic cross section of a 100 mm reinforced concrete cube specimen

Chloride-Induced Corrosion (in Uncracked Concrete)

Resistance of uncracked concrete to chloride-induced reinforcement corrosion was determined in accordance with test procedures developed at the University of Dundee (Dhir *et al*, 1995). As for

the carbonation-induced corrosion test, two very similar 100 mm cube specimens were used hence the same procedure was followed in their preparation except for curing, where the specimens were water-cured at 20°C for 28 days. After curing, the specimens were dried (20°C, 55% RH) for 5 days and sealed except for the test face. For each mix, three 100 mm plain concrete cubes were also cast with the reinforced concrete specimens to determine the water-soluble and total chloride ion contents at different exposure periods during the test. All specimens were exposed to cycles of 6 hours wetting with 2 molar (M) sodium chloride solution at 20°C, followed by 6 hours drying (20°C). Corrosion potential and polarisation resistance measurements were taken immediately prior to, and periodically during the chloride exposure. After 80 weeks of exposure, the cubes were split and a visual assessment was made on the recovered reinforcement.

Chloride-Induced Corrosion (in Cracked Concrete)

Resistance of cracked concrete to chloride-induced reinforcement corrosion was monitored using 100 x 100 x 475 mm beam specimens with a 10 mm diameter steel bar located at a concrete cover of 45 mm. For each crack width, two or three specimens were used. Steel bars of length 500 mm were prepared as for the 100 mm cube specimens, but leaving a longer exposed length (350 mm) at the centre. Each specimen was cast with only one bar (the working electrode) as an aluminium foil was placed above the concrete specimen to act as the counter electrode (the secondary electrode), while testing. Prior to casting, the steel bar was placed in a steel mould using two pre-drilled plywood sheets located at the two ends and, then, secured using silicon. After demoulding, the protruding bars were coated with pitch epoxy resin and the specimens were water-cured (20°C) for 28 days, together with a 100 mm plain concrete cube (for each mix), which was used to determine the initial chloride content (water-soluble). The specimens were, then, dried (20°C and 55% RH) for 7 days and coated with silane primer except the uppermost face at casting.

Thereafter, each specimen was loaded using a stainless steel loading arrangement until a crack (intersecting) appeared at the upper central portion. To achieve this, each specimen was clamped against a roller support resting on a channel section and loaded by tightening the nuts at the top. Figure 3.6 shows details of the test specimen and the loading arrangement. The crack width was observed using an electrical microscope, while loading. The vertical sides of the specimens were sealed with two coats of pitch epoxy resin, allowing chloride ingress to the crack zone to occur through the top surface only. After the epoxy resin hardened, the load maintained specimens were exposed to alternate 6 hours wetting with 3.5% sodium chloride solution at 20°C (to simulate sea water) and 6 hours drying (20°C) cycles. Corrosion potential and polarisation resistance measurements were taken immediately prior to the chloride exposure and continued throughout the test period (10 weeks). At every week, crack widths were microscopically examined and maintained by loading to avoid any effects due to healing. After 1, 4 and 10 weeks of exposure,

one specimen for each crack width (selectively) was drilled (at both cracked and uncracked zones) to find the water-soluble chloride content at depths 30 and 45 mm. As the drilling was destructive, reinforcement bars were recovered for visual assessment.

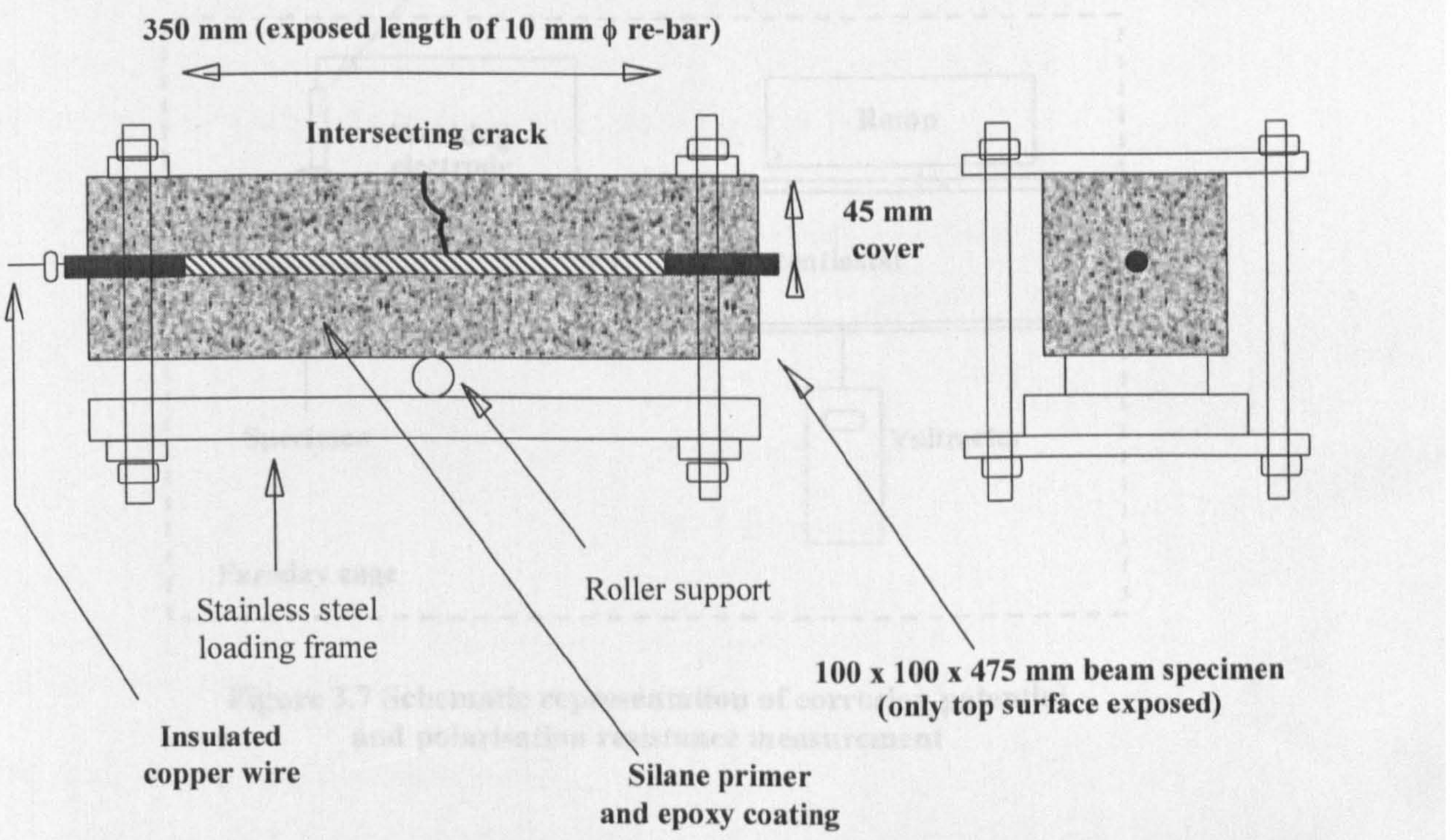


Figure 3.6 Loading arrangement and details of a reinforced concrete beam specimen

3.6.6 Assessment of Reinforcement Corrosion

Corrosion Potential (E_{corr})

Corrosion potential was measured using a Sycopel potentiostat (DD10M1) and a standard silver / silver chloride reference electrode, following the guidelines given in ASTM C 876 (ASTM, 1991). The measurement was preliminary to polarisation resistance determination and the equipment layout is shown in Figure 3.7. As the test equipment was sensitive to interference from other electrical instruments in the laboratory, it was located in a Faraday cage in order to provide a shield against extraneous noise. The reference electrode was placed on the concrete surface (centrally for the 100 mm cube specimens and above the crack for the beam specimens) and a good contact was achieved between them using a sponge soaked in detergent solution, positioned at the probe / concrete interface. Connections were made between the electrodes (reference, working and counter) and the potentiostat using screened heads. The corrosion potential (mV) was directly recorded with a stable reading normally obtained within 5 minutes. At regular intervals, the

reference electrode was checked for reliability against a standard calomel reference electrode and the electrolyte was changed, as required (at least two monthly).

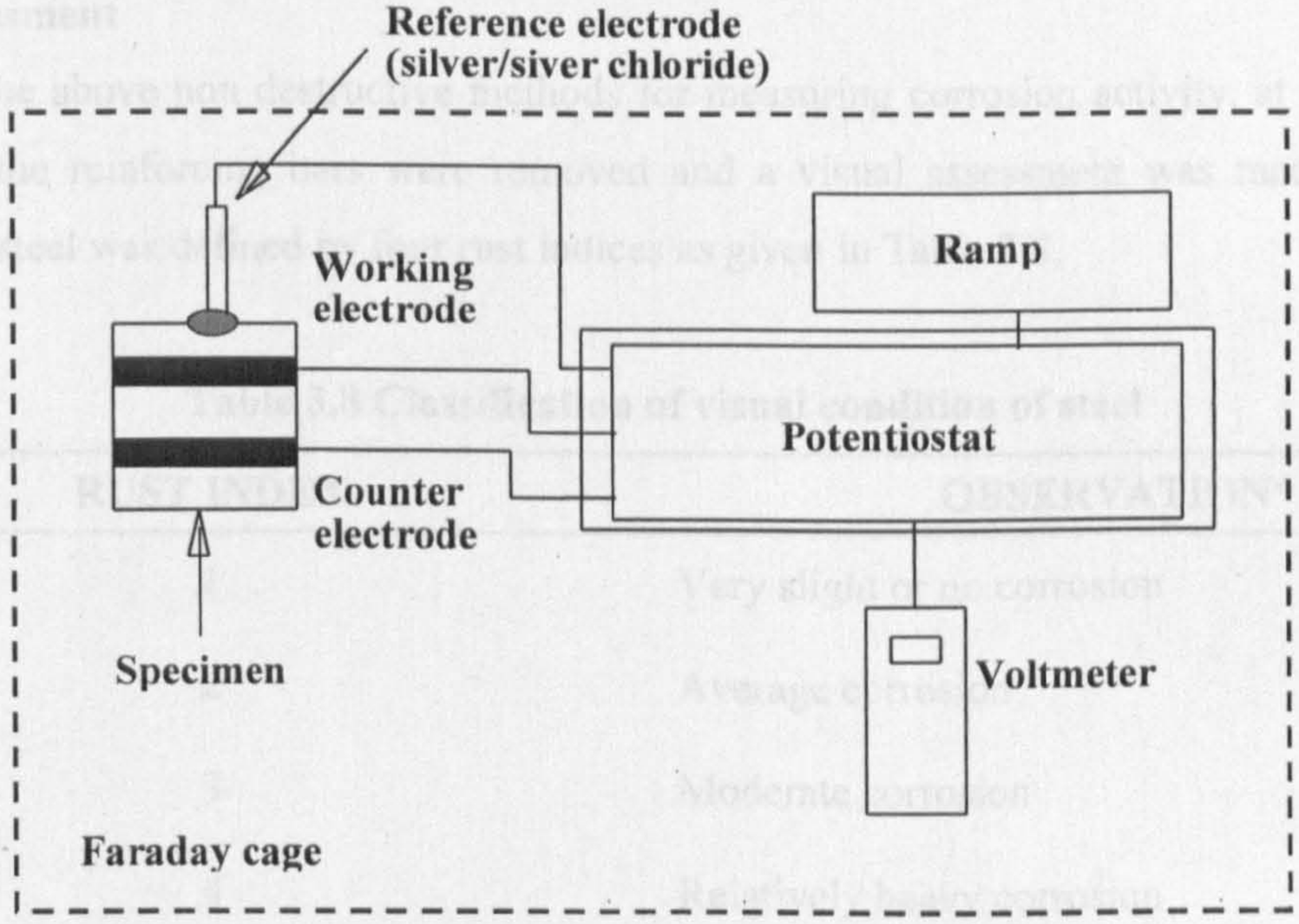


Figure 3.7 Schematic representation of corrosion potential and polarisation resistance measurement

Polarisation Resistance (R_p)

After determining the corrosion potential, the potentiostat was set to enable polarisation of the steel with respect to the measured potential value. The potentiostat was equipped with a positive feedback IR compensation. This is required to take account of the electrolytic resistance of the concrete between the reference and working electrode and provides a voltage increment proportional to the required compensating resistance, which is added to the applied potential during the subsequent potential sweep. The IR compensation was switched on and the steel was, then, polarised over a range of ± 10 mV from E_{corr} at a rate of 6 mV/minute. The output from the potentiostat was recorded using a milli-voltmeter at 1 mV increments. Two sets of readings were taken, one with decreasing polarised potential and the other with increasing polarised potential. The measured voltages (mV) were converted to currents (mA) using the resistor value for the voltage setting of the potentiostat. The applied voltage was plotted against the output current and, from the slope of the best fitting straight line, the polarisation resistance (mΩ) was calculated. The corrosion current (I_{corr}) was calculated in mA, from the simplified version of the Stern-Geary equation, *i.e.*

$$I_{corr} = B / R_p$$

where, B is 26 mV for steel in corroding conditions. The I_{corr} value was divided by the exposed surface area of the steel bar in order to find corrosion current density, which was expressed in $\mu A/cm^2$. The corrosion current densities were converted to more practical corrosion rates using

Faraday's law, as suggested by Broomfield (1997). This converts 1 $\mu A/cm^2$ to 11.6 μm of steel loss per year.

Visual Assessment

To support the above non destructive methods for measuring corrosion activity, at the end of the test period, the reinforcing bars were removed and a visual assessment was made. The visual condition of steel was defined by four rust indices as given in Table 3.8.

Table 3.8 Classification of visual condition of steel

RUST INDEX	OBSERVATION*
1	Very slight or no corrosion
2	Average corrosion
3	Moderate corrosion
4	Relatively heavy corrosion

** At the end of the test period*

3.6.7 Determination of Chloride Content

Both total and water-soluble chloride contents were determined using powder samples taken from the concrete specimens, removed from chloride tanks at different times during the exposure period. For the uncracked cube specimens, samples were obtained from the sacrificial plain concrete specimens except the last one, which was taken from the reinforced concrete specimens at the end of the exposure period. Sampling was made from the reinforced concrete beam specimens directly at the cracked and uncracked zones. Firstly, the layer of wax and any salt crystals deposited on the specimens were removed using a wire brush and a scraper. Then, the specimens were lightly washed and surface dried. For the cube specimens, 5 mm thick concrete slices were cut parallel to the exposed face at required depths (15, 25 and 35 mm) and carefully crushed using a hammer before ball milling for 10 minutes until passing a 150 μm sieve. For the beam specimens, drilling was done perpendicular to the exposed face using a 20 mm diameter masonry drill and the samples were taken in a region of $\pm$ 2.5 mm from the required depths (30 and 45 mm), prior to ball milling.

Total Chloride Content

X-ray fluorescence spectrometry (XRFS) was used to determine the percentage total chloride content of the powdered concrete samples using a calibrated, Phillips PW 1410 X-ray spectrometer, see Figure 3.8. Approximately 5 g of powdered sample was put into an aluminium cup and, then,

compressed in a hydraulic press under a load of 100 kN for 5 minutes to produce a 30 mm diameter, pressed powder pellet. These pellets were directly used for testing.

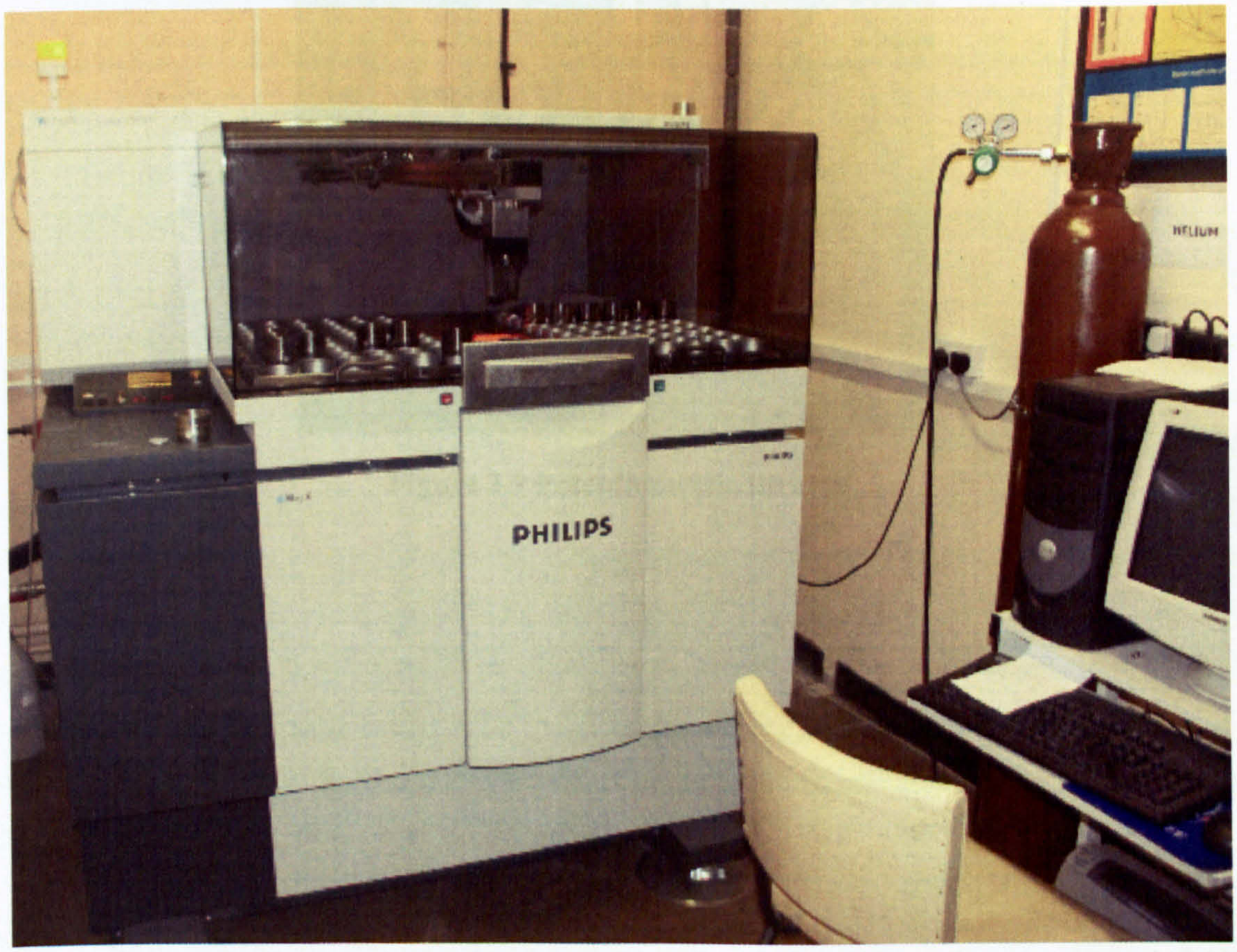


Figure 3.8 X-ray spectrometer

Water-Soluble Chloride Content

A method recommended by Dhir *et al* (1990b) was used to extract chloride ions into the solution and a potentiometric titration method with silver nitrate (716 Titrino instrument) was used to determine the water-soluble chloride content. A photograph of the potentiometric titrator is shown in Figure 3.9. Firstly, a 5 g of powdered sample was mixed with 100 ml of distilled, de-ionised water. The mixture was boiled for 5 minutes and left covered for 24 hours to allow settling of the particles. A 5 ml aliquot of liquid sample was taken using a pipette, without any powder at the bottom and added to a small beaker. This was mixed with 1 ml of 10% nitric acid and 40 ml of distilled, de-ionised water prior to titration. At the end-point, the chloride content in the 5 ml sample (in ppm) was directly recorded.

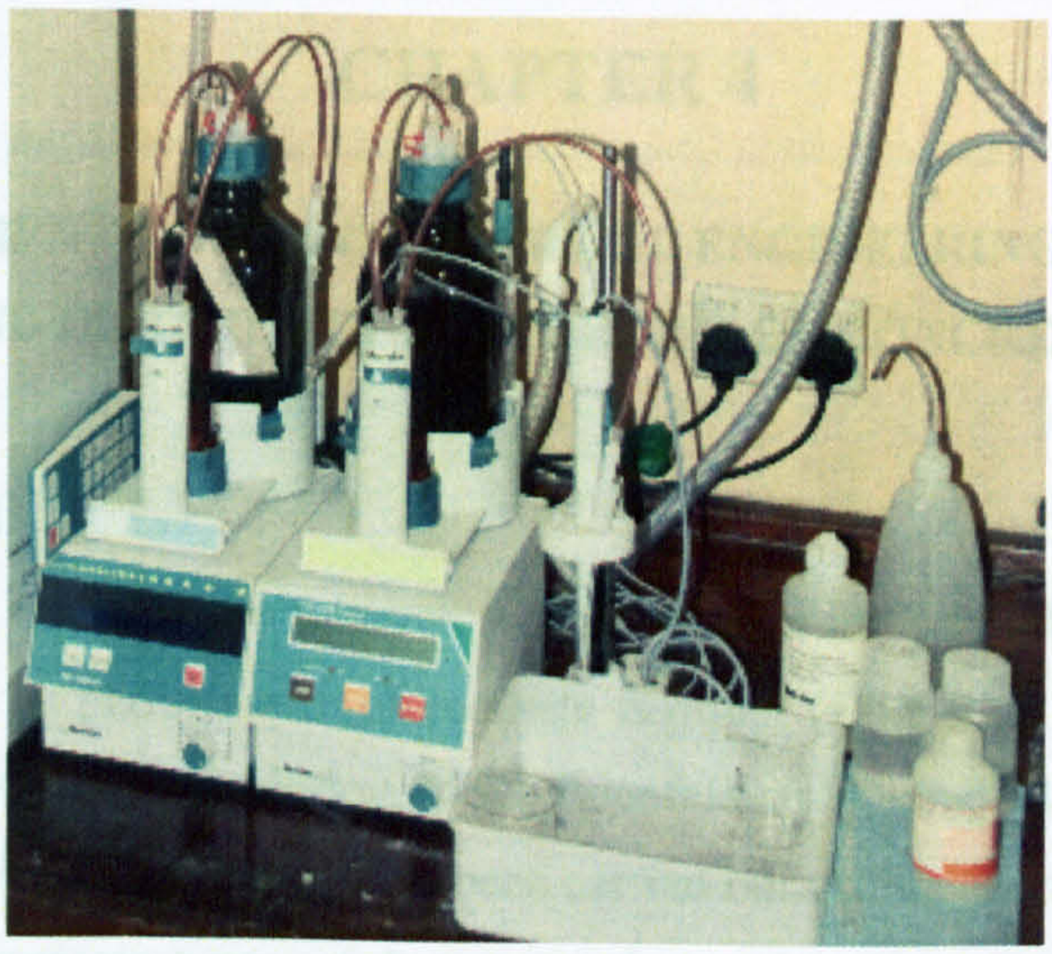


Figure 3.9 Potentiometric titrator

CHAPTER 4

ROLE OF CEMENT CONTENT ON FRESH, ENGINEERING, PERMEATION AND DURABILITY PROPERTIES OF CONCRERTE

4.1 INTRODUCTION

As noted in Chapter 2, much of the research in the literature indicates that at fixed w/c ratio, the role of cement content on performance of concrete is minor (Dhir *et al*, 1987a; Dhir *et al*, 1991; Monteiro *et al*, 1993; Mangat and Molloy, 1995; Buenfeld and Okundi, 1998). However, it should be noted that the majority of this work have been carried out using commonly available, relatively low porosity coarse aggregate types, such as natural gravel and crushed granite. Indeed, a wide range of aggregate types is being used in concrete practice. However, it appears that aggregate characteristics are often overlooked in the current specifications for concrete durability (BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002)). Therefore, dolomitic magnesium limestone, which has a relatively high water absorption reflecting its higher porosity and high aggregate impact (AIV) and crushing values (ACV) indicating its slightly lower resistance to pulverisation, compared to the aggregates commonly tested in the literature, was selected as the major coarse aggregate type for the study.

This stage of the project was designed to investigate the influence of cement content at fixed w/c ratio on the fresh, engineering, permeation and durability properties of concrete made with PC, 42.5 N cement and dolomitic magnesium limestone coarse aggregate. In addition to PC / limestone combination, selected permeation properties were tested for concrete made with a range of coarse aggregate and cement types to cover a range of material properties and qualities currently in use, since most durability properties of concrete and its resistance to reinforcement corrosion are closely related to these.

However, it is beyond the scope of this stage to cover the influence of coarse aggregate and cement type in assessing the role of cement content, in the specification for durability of concrete. (For a more detailed review of these, see previous work carried out by Zhou (2001) and Menzies (2002) for the influence of coarse aggregate type and cement type, respectively).

The experimental programme of study including concrete mix details, curing conditions and properties tested, was discussed in Chapter 3, in Stage 1 (fresh, engineering, permeation and durability properties of concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse

aggregate) and Stage 2 (selected permeation properties of concrete made with a range of coarse aggregate and cement types).

4.2. FRESH PROPERTIES

Cohesion and finishability were tested for all concrete mixes made at all four w/c ratios (0.65, 0.55, 0.50 and 0.45). Air content measurements were carried out on fresh concrete for those mixes tested for freeze / thaw (scaling) resistance, *i.e.* all seven mixes at w/c ratio 0.45. Bleeding tests were carried out at w/c ratio 0.55 for Mixes M5, M1, M3*f* (filler included) and M3.

4.2.1 Cohesion

The classifications used for assessment of the cohesion property of fresh concrete are given in Table 3.6. The cohesion results are given in Table 4.1. For a given w/c ratio;

- The cohesion of the Reference Mix (M1) was assessed as class 2b (*i.e.* cohesive).
- With the use of filler to maintain the fines content equal to that of the Reference Mix (M1), a 20 l/m^3 water (and corresponding cement) reduction (M2*f*) resulted in no change to the cohesion of the mix compared to the Reference Mix (M1), but with a further 20 l/m^3 water reduction (M3*f*), generally, there was a tendency for slight loss of cohesion. Where the filler was omitted, a 20 l/m^3 water reduction (M2) had no effect on cohesion compared to the Reference Mix (M1). However, with a 40 l/m^3 water reduction (M3), considerable cohesion loss was observed giving a classification of 2c (little cohesion).
- Very cohesive mixes (class 2a) were obtained when water (thus, cement) content was increased (M5), giving increased workability (from 75 to 180 mm nominal slump), or when the workability was raised from 75 to 180 mm nominal slump through the use of superplasticizer (M4).

Cohesion is the ability to bind concrete materials together and good cohesion limits the likelihood of segregation. The reason for the reduction in cohesiveness, as mainly noted for M3 Mixes, can probably be attributed to the reduced level of cement paste to cover and bind the increased aggregate content (due to cement reduction) and to fill the space between larger particles. This effect was mitigated to some extent when limestone filler was included to maintain the fines content, hence the paste (cement plus filler) content, equal to the Reference Mix (M1). In addition, high superplasticizer levels used in Mixes M3 and M3*f*, may result in locally excessive wet regions in concrete, which may lead to segregation. Obviously, the very cohesive nature of M5 Mixes reflects the increased cement paste volume. There probably were differences between Mixes M5 and M4 in terms of cohesion, but due to the simple test method employed, these were not detected.

4.2.2 Finishability

The classes used to assess finishability are defined in Table 3.7 and the data obtained are given in Table 4.1, together with other fresh properties. At a given w/c ratio;

- Reference Mix (M1) exhibited good finishability characteristics and a smooth finish was obtained with moderate effort (*i.e.* class 2).
- Compared to the Reference Mix (M1), a 20 l/m^3 water (and corresponding cement) reduction with the inclusion of filler, *i.e.* Mix M2*f*, had no effect on finishability characteristics. Whilst for Mix M3*f* (a further 20 l/m^3 water reduction), there was a tendency for a slight adverse effect on finishability in comparison to the Reference Mix (M1) and was assessed as being of class 2 to 3. Where the filler was omitted, a water reduction of 20 l/m^3 (M2) had no practical significance on finishability compared to the Reference Mix (M1). However, a 40 l/m^3 water reduction (M3) resulted in unacceptable finishability (*i.e.* class 3).
- Increasing water (hence cement) content (M5) with workability increase (from 75 to 180 mm nominal slump), or raising workability from 75 to 180 mm nominal slump through the use of superplasticizer (M4), generally led to improved finishability compared to the Reference Mix (M1), although this effect was less pronounced at lower w/c ratios.

The ability to achieve the required surface finish of concrete is closely related to the cohesive nature of concrete. With large reductions in cement and water contents, for example, M3 Mixes, difficulties in achieving a smooth finish are possibly due to insufficient cement paste and fine material to cover the increased aggregate content (due to cement reduction) and fill the voids between them. This is likely to be offset by the inclusion of limestone filler with the increased paste content and improved particle packing (due to increased fineness of the filler). As for the cohesion, increased cement and water contents (hence the cement paste content) are likely to improve the finishability characteristics of M5 Mixes. Slightly better finishability of M4 Mixes may be due to better deflocculation and dispersion of cement particles with the inclusion of superplasticizer and reduced coarse aggregate content in the mix to accommodate the increased workability.

4.2.3 Air Content

Table 4.1 gives the air content results (% by volume of concrete) obtained for concrete (non-air entrained) at w/c ratio 0.45. The results indicate that at w/c ratio 0.45;

- The Reference Mix (M1) resulted in an air content of 1.7%.
- Air content was not influenced significantly compared to the Reference Mix (M1), by reduction in cement (and, thus, water) content either with (M2*f*, M3*f*) or without (M2, M3) the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix (M1).

- Increasing cement (hence water) content with workability increase from 75 to 180 mm nominal slump (M5), or raising workability from 75 to 180 mm nominal slump through the addition of superplasticizer (M4), had a minor influence on air content compared to the Reference Mix (M1).

Table 4.1 Fresh properties (except bleeding) of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	FRESH PROPERTY: PLASTIC DENSITY, kg/m^3	COHESION	FINISHABILITY	AIR CONTENT, % by volume
0.65	M5*	2320	2a	1 to 2	n/t
	M4*#	2370	2a	1 to 2	n/t
	M1	2360	2b	2	n/t
	M2*f*#	2385	2b	2	n/t
	M2#	2385	2b	2	n/t
	M3*f*#	2405	2b	2 to 3	n/t
	M3#	2390	2c	3	n/t
0.55	M5*	2335	2a	1 to 2	n/t
	M4*#	2370	2a	1 to 2	n/t
	M1	2370	2b	2	n/t
	M2*f*#	2390	2b	2	n/t
	M2#	2395	2b	2	n/t
	M3*f*#	2425	2b to 2c	2 to 3	n/t
	M3#	2420	2c	3	n/t
0.50	M5*	2360	2a	1 to 2	n/t
	M4*#	2375	2a	2	n/t
	M1	2385	2b	2	n/t
	M2*f*#	2400	2b	2	n/t
	M2#	2405	2b	2	n/t
	M3*f*#	2425	2b to 2c	2 to 3	n/t
	M3#	2430	2c	3	n/t
0.45	M5*	2340	2a	2	1.5
	M4*#	2380	2a	2	1.2
	M1	2380	2b	2	1.7
	M2*f*#	2410	2b	2	1.7
	M2#	2395	2b	2	1.5
	M3*f*#	2435	2b to 2c	2 to 3	1.7
	M3#	2410	2c	3	1.8

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

The reduced volume of cement paste with cement and water reduction may contribute to reduce the air content in concrete as air bubbles are entrained only in the cement paste. However, this effect may be weakened by the increased aggregate content due to increased resistance to movement or escape of air bubbles during compacting. The inclusion of limestone filler increases the paste (cement plus filler) content, which may support an increased air content. On the other hand, improved particle packing due to high fineness of the filler may contribute to reduce the pore space and air content. As the porosity of limestone aggregate is high, it is possible to increase the air content of concrete with cement and water reduction (thus, increasing aggregate content) if the aggregates do not absorb water to saturated surface dry condition before testing. However, this effect was eliminated by applying aggregate correction factors, as stated in the Standard (BS 1881: Part 106 (1983)). Some superplasticizing admixtures have the additional effect of entraining air, in addition to plasticizing action. However, the results suggest that chemical admixture did not entrain air. Overall, it appears that variation in cement and water contents at fixed w/c ratio has no significant effect on the air content of concrete.

It is also worth noting that air contents given in Table 4.1, are expressed as percentages by volume of concrete but, as mentioned earlier, air is entrained mainly in the cement paste. Thus, if air contents are given as percentages by volume of cement paste, reducing cement and water contents tends to increase air content significantly (Mixes M3, M4 and M1 resulted in air contents of 7.3% (highest), 3.8% (lowest) and 5.4%, respectively).

4.2.4 Bleeding

The cumulative bleeding results (% by mass of free water, 2 hours after mixing) and bleeding initiation times are given in Tables 4.2 (a) and (b), respectively, for concrete mixes of w/c ratio 0.55. The cumulative quantities of bleed water (% of free water) are plotted against bleed time in Figure 4.1. The results indicate that at w/c ratio 0.55;

- The Reference Mix (M1) gave no bleed water with in the first 10 minutes of testing. After 2 hours, total bleeding was 0.8% by mass of free water in the test sample.
- Bleeding tended to start later for mixes having reduced water (and, thus, cement) contents, *e.g.* for Mix M3, bleeding initiated after 60 minutes of mixing and, at a given test time, cumulative bleeding (relative to the free water in the test sample) was significantly lower than that of the Reference Mix (M1). After 2 hours, recorded cumulative bleeding was just 13% of that of the Mix M1. When the filler was included to maintain the fines content (M3*f*), no bleed water was collected over the 2 hour test period.
- When water (thus, cement) content was increased, with increased workability from 75 to 180 mm nominal slump (M5), bleeding tended to increase. For this mix, after 2 hour test period, total bleeding was increased by 225% compared to the Reference Mix (M1).

Table 4.2 Bleeding of concrete made with dolomitic magnesium limestone coarse aggregate

(a) Cumulative bleeding

W/C RATIO	MIX	CUMULATIVE BLEEDING (2 HOURS)	
		% of free water in sample (by mass)	% of M1
0.55	M5*	1.8	225
	M1	0.8	100
	M3*f*#	0.0	0
	M3#	0.1	13

(b) Initiation of bleeding

W/C RATIO	MIX	BLEEDING INITATION TIME	
		Minutes	% of M1
0.55	M5*	0	0
	M1	10	100
	M3*f*#	no bleeding	no bleeding
	M3#	60	600

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

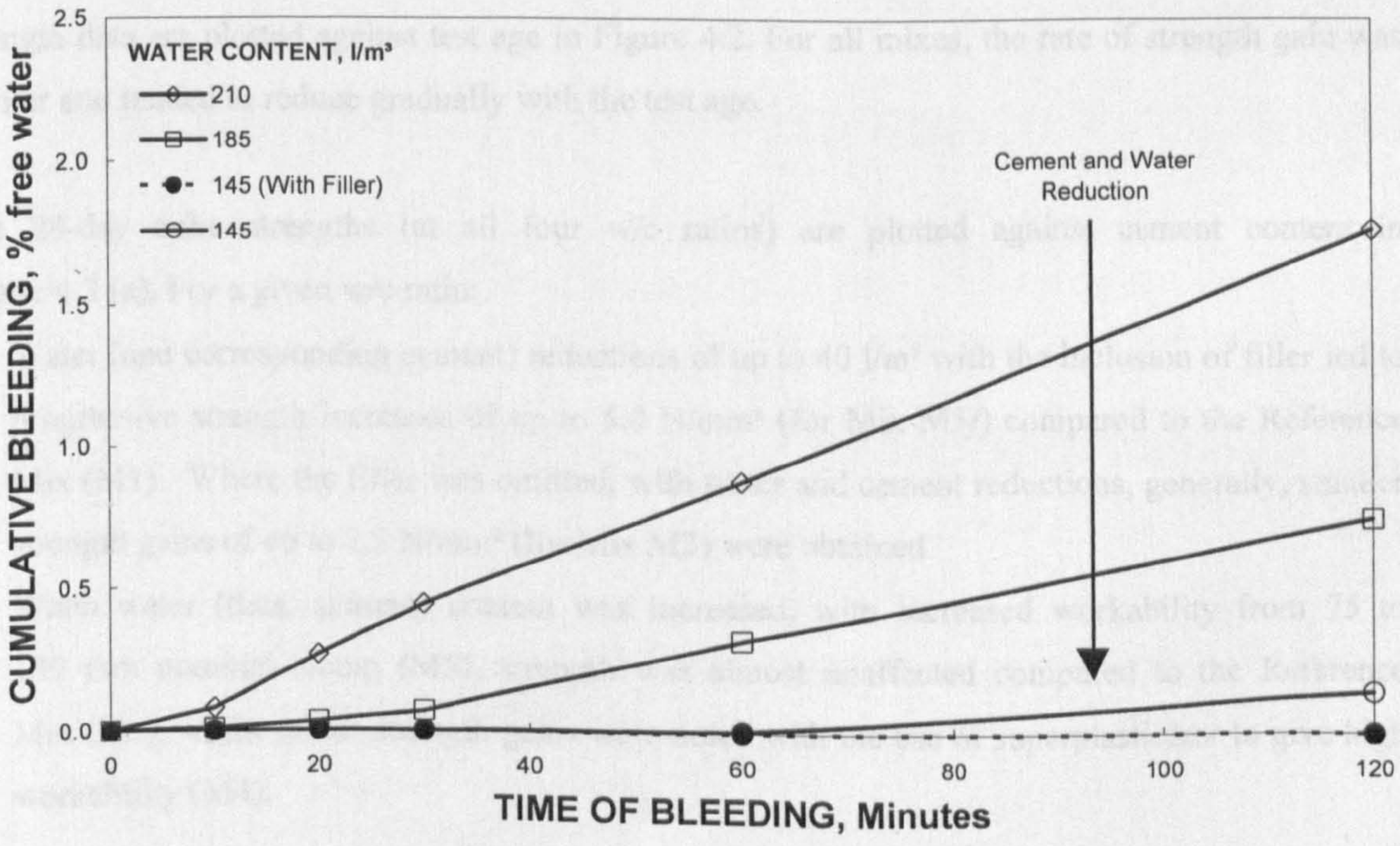


Figure 4.1 Cumulative bleeding of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.55

Bleeding is significant as it represents a form of segregation, which can lead to non uniform properties (in terms of vertical profile) in concrete. Obviously, the reduced bleeding with water (hence cement) reduction is likely to be due to less water available in concrete for bleeding. Bleeding occurs within the cement paste, while the aggregates tend to block bleed water movements. With reduction in cement and water contents in equal proportion, the volume of aggregate increases, while that of cement paste reduces and, possibly, this also causes reduced bleeding. The addition of fine limestone filler improves particle packing and, therefore, is likely to reduce bleeding due to increased blocking and tortuosity of bleed channels. In addition, absorption and adsorption properties of limestone filler (see Section 4.3.1 on the compressive strength) probably reduce the water available for bleeding.

4.3 ENGINEERING PROPERTIES

All concrete mixes made at all four w/c ratios (0.65, 0.55, 0.50 and 0.45) were tested for compressive (cube) strength development up to the age of 180 days. Flexural strength tests were carried out for all seven mixes at w/c ratios 0.65 and 0.55, and for Mixes M5, M1, M3*f* and M3 at w/c ratio 0.45. The modulus of elasticity and load to failure tests were carried out at w/c ratio 0.55 for all seven mixes and selected number of mixes (M5, M1, M3*f* and M3), respectively. Drying shrinkage measurements were made on concrete specimens at w/c ratio 0.55 for all seven mixes.

4.3.1 Compressive Strength

Table 4.3 gives the compressive strength development data of 100 mm cube specimens, water-cured (20°C) up to the age of 180 days. As a typical example, for mixes at w/c ratio 0.50, the strength data are plotted against test age in Figure 4.2. For all mixes, the rate of strength gain was similar and tended to reduce gradually with the test age.

The 28-day cube strengths (at all four w/c ratios) are plotted against cement content in Figure 4.3 (a). For a given w/c ratio;

- Water (and corresponding cement) reductions of up to 40 l/m³ with the inclusion of filler led to progressive strength increases of up to 5.0 N/mm² (for Mix M3*f*) compared to the Reference Mix (M1). Where the filler was omitted, with water and cement reductions, generally, smaller strength gains of up to 2.5 N/mm² (for Mix M3) were obtained.
- When water (thus, cement) content was increased, with increased workability from 75 to 180 mm nominal slump (M5), strength was almost unaffected compared to the Reference Mix (M1), whilst minor strength gains were noted with the use of superplasticizer to give high workability (M4).

Figure 4.3 (b) shows that whilst the relationship between compressive strength and w/c ratio was influenced by variation in cement and water contents in equal proportion, w/c ratio remained the main influencing factor for strength. For example, increasing the w/c ratio of the Reference Mix (M1) from 0.50 (370 kg/m³ cement) to 0.55 (335 kg/m³ cement), led to a strength reduction of 4.0 N/mm² (9%), whilst a similar reduction in cement content at fixed w/c ratio 0.55, *i.e.* from 335 kg/m³ (Mix M1) to 300 kg/m³ (Mix M2*f*), resulted in a strength gain of only 2.0 N/mm² (5%).

Table 4.3 Compressive strength development of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	PC, 42.5 N kg/m³	FREE WATER l/m³	CUBE STRENGTH N/mm²					% of 28-d strength					% of M1
				3-d	7-d	28-d	90-d	180-d	3-d	7-d	28-d	90-d	180-d	28-d
0.65	M5*	323	209	17.0	23.5	33.5	39.0	42.5	51	70	100	116	127	99
	M4*#	283	184	19.0	25.0	36.0	40.0	43.0	53	69	100	111	119	106
	M1	283	184	19.0	24.0	34.0	41.5	43.0	56	71	100	122	126	100
	M2*f*#	254	164	21.0	26.5	35.5	40.5	42.5	59	75	100	114	120	104
	M2#	254	164	19.0	25.0	33.0	39.0	40.5	58	76	100	118	123	97
	M3*f*#	224	144	22.5	28.5	37.5	42.5	43.5	60	76	100	113	116	110
	M3#	224	144	21.0	27.0	34.5	42.0	43.0	61	78	100	122	125	101
0.55	M5*	379	210	21.5	29.0	40.0	46.5	50.5	54	73	100	116	126	101
	M4*#	334	185	24.0	31.0	42.0	47.5	50.0	57	74	100	113	119	106
	M1	334	184	23.0	28.5	39.5	48.5	51.0	58	72	100	123	129	100
	M2*f*#	299	165	26.5	32.5	41.5	48.0	51.0	64	78	100	116	123	105
	M2#	299	165	25.0	31.0	40.0	46.0	48.0	62	78	100	115	120	101
	M3*f*#	265	145	28.5	34.5	44.0	50.5	51.5	65	78	100	115	117	111
	M3#	265	145	27.0	34.0	41.0	50.0	51.0	66	83	100	122	124	104
0.50	M5*	420	210	24.5	33.5	44.0	51.0	55.0	56	76	100	116	125	101
	M4*#	370	185	28.0	35.0	46.5	51.5	54.0	60	75	100	111	116	107
	M1	370	185	26.5	32.5	43.5	53.0	55.0	61	75	100	122	126	100
	M2*f*#	330	165	30.5	37.0	46.0	53.0	56.0	66	80	100	115	122	106
	M2#	330	165	29.0	34.5	44.0	51.5	53.5	66	78	100	117	122	101
	M3*f*#	290	145	32.5	39.0	48.5	55.5	57.5	67	80	100	114	119	111
	M3#	290	145	31.5	38.0	46.0	55.0	57.0	68	83	100	120	124	106
0.45	M5*	467	211	28.5	38.5	50.5	56.0	60.0	56	76	100	111	119	100
	M4*#	411	185	32.0	40.0	53.0	57.0	59.0	60	75	100	108	111	105
	M1	411	185	30.5	38.5	50.5	56.5	58.5	60	76	100	112	116	100
	M2*f*#	366	165	36.0	42.5	52.5	59.0	62.0	69	81	100	112	118	104
	M2#	366	165	34.5	40.5	50.0	57.0	58.5	69	81	100	114	117	99
	M3*f*#	321	145	38.0	45.0	55.5	62.5	64.0	68	81	100	113	115	110
	M3#	321	145	36.5	43.0	51.5	60.0	62.0	71	83	100	117	120	102

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

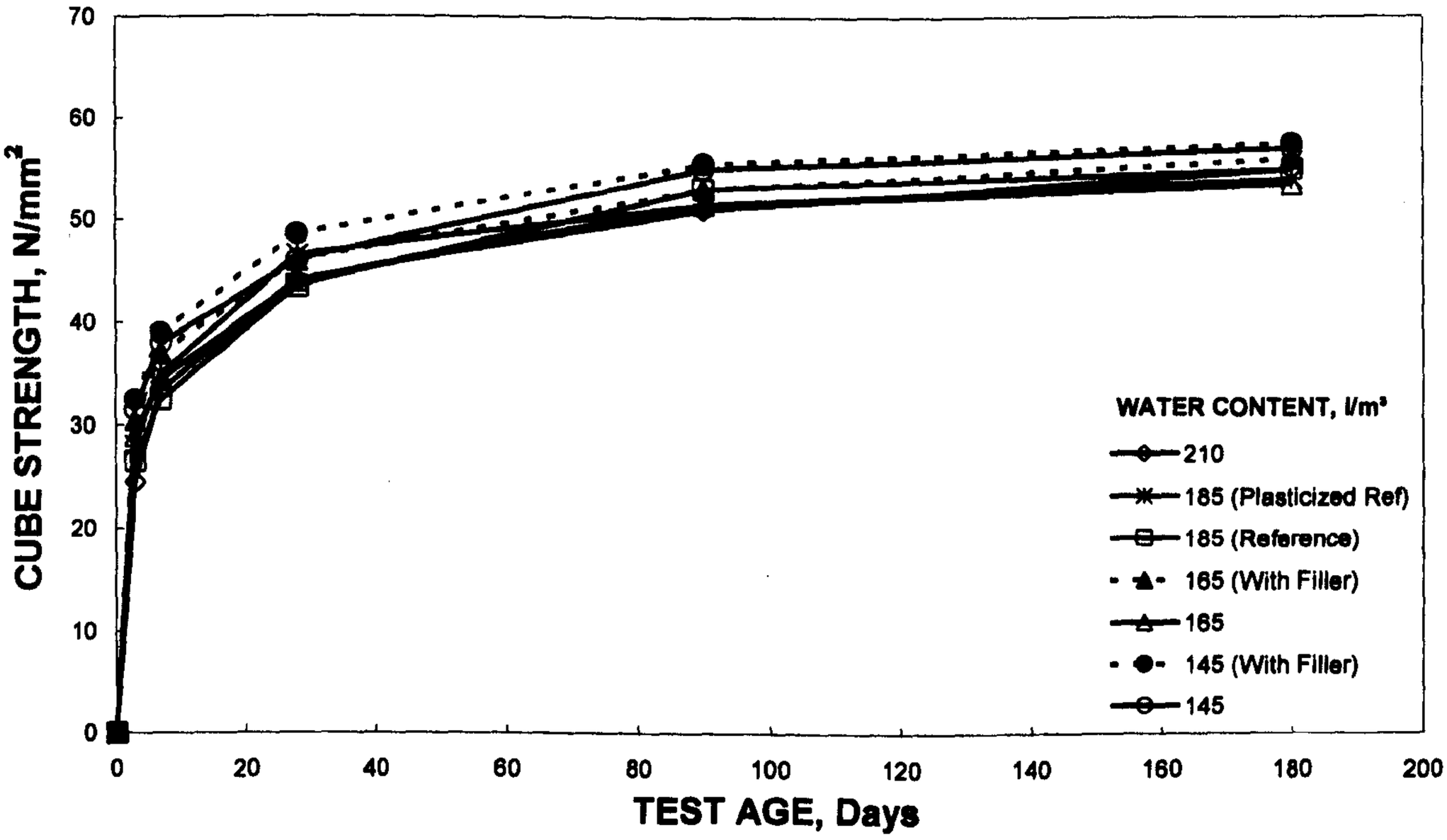


Figure 4.2 Compressive strength development of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.50

The above trends are in line with most of the relevant literature (see Section 2.4.2 in Chapter 2) and can be attributed to several factors occurring in combination.

By reducing cement and water contents in equal proportion, the volume of aggregate (both total and coarse) is increased and the volume of cement paste is reduced. Therefore, increasing strength with cement and water reduction demonstrates that porosity of the combined aggregate (mainly consists of coarse aggregate) in concrete is lower than that of the hardened cement paste in concrete. Consequently, it suggests that reducing cement and water contents in equal proportion reduces the amount of voids in concrete (total porosity of concrete), thereby increasing strength. In addition, reducing w/c ratio results in reduced porosity of cement paste (and, therefore, concrete), thus, increased strength. This effect appears to be more pronounced with reducing w/c ratio than cement and water contents in equal proportion, as the results (which agree with relevant literature) indicate that w/c ratio remained the main influencing factor for strength, not the cement content. A more detailed review of this subject is given in Zhou (2001), where the effect of total porosity on a range of concrete properties is examined.

Reducing cement and water contents in equal proportion results in higher aggregate concentrations. Increasing aggregate, which is stiffer than cement paste, possibly results in higher compressive strengths. Indeed, it has been found that when aggregate is much stiffer than cement paste, increasing aggregate volume concentration from 65 to 75% leads to an increase in strength

by 6% (Hobbs, 2001). In addition, when there is less paste to cover the increased surface area of aggregates, they tend to contact particle-to-particle physically, increasing strength in compression (Jones and Kaplan, 1957). Moreover, due to the higher porosity of limestone, cement paste is more likely to be absorbed into the aggregates (Zhang and Gjorv, 1990) and limestone aggregates may react with PC hydration products (Monteiro and Mehta, 1986; Tasang *et al*, 1998). Both these mechanisms may also contribute to increased compressive strength of concrete.

Increasing strength in cement-and-water-reduced concrete mixes containing filler is, perhaps, the most noticeable feature of the compressive strength results. The observed behaviour is probably due to enhanced hydration of cement particles due to increased nucleation sites provided by the filler (Neville, 1995; Detwiler and Tennis, 1996). In addition, the very small particle size of the filler can improve particle packing, leading to a denser microstructure with reduced capillary pores and hence to a higher strength (Soroka and Setter, 1977; Larrard, 1989). Furthermore, limestone filler may react with PC hydration products and lead to increased strength, though this is generally thought to be of fairly limited importance (Detwiler and Tennis, 1996). Another aspect of limestone filler is its possibility to absorb and adsorb water, thereby reducing the free w/c ratio of concrete, leading to increased strength. Indeed, it has been suggested (Menzies, 2002) that limestone may absorb and adsorb water between 10 and 25% by its mass.

The inclusion of superplasticizer leads to better deflocculation and dispersion of cement particles and, consequently, better hydration of cement and better compaction of concrete (Neville, 1995). This can probably support an increase in the compressive strength to a limited extent as can be seen comparing the results of Mixes M1 and M4. This effect may also have supported the strength improvement of cement-and-water-reduced concrete mixes as they contained high superplasticizer levels, though it is not possible to isolate this from the mechanisms discussed earlier.

It should be noted that increased strength of cement-and-water-reduced mixes is also likely to be associated with reduced bleeding. This tends to eliminate water collection below aggregates, which can create locally higher w/c ratios and, thus, porous weak zones (Subramanian, 1999). In addition, it forms less bleed channels to the concrete surface, which are again zones of higher w/c ratio (Neville, 1995).

It is also worth mentioning that for each 1% increase in entrained air, the compressive strength drops by 5% (Neville, 1995). However, as the air content was not influenced significantly by reduction in cement and water contents in equal proportion (see Section 4.2.3), its influence on compressive strength (in this case) appears to be negligible.

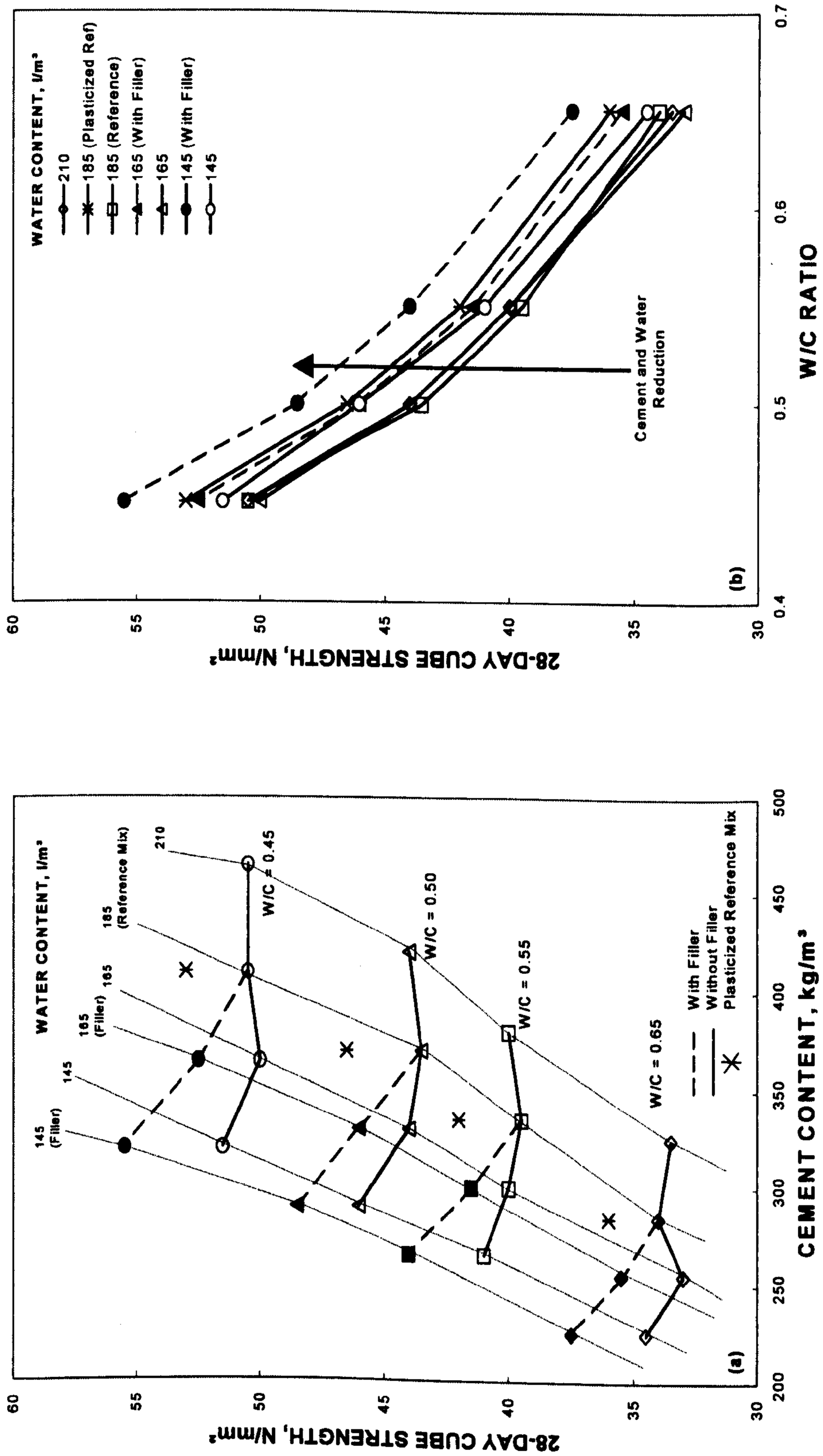


Figure 4.3 Effect of cement content on compressive strength of concrete made with dolomitic magnesium limestone coarse aggregate

In addition, reduction in cement and water contents in equal proportion may be expected to have an influence on the aggregate-cement paste interfacial transition zone (ITZ), which is known to be the weakest part of the composite. Indeed, increasing aggregate content (and reducing cement content) should increase the effective interfacial zone area. Similarly, as the aggregate content increases, there will be greater continuity of the ITZs (Winslow *et al*, 1994). However, Zhou (2001), using back-scattered scanning electron microscopy (SEM), concluded that there was no change in the ITZ thickness between the Reference Mix (M1) and the cement-reduced mix with limestone filler, *i.e.* M3*f* (for concrete made with natural gravel coarse aggregate). Therefore, overall, it is difficult to establish that the observed trends are due to changes occurring in ITZ with cement and water reduction in equal proportion, or this effect on strength may be minor.

4.3.2 Flexural Strength

The flexural strength data with flexural strength / compressive strength ratios are given Table 4.4. Figures 4.4 (a) to (c) show the relationships of flexural strength with cement content, w/c ratio and 28-day cube strength, respectively. In general, the results are in line with previous studies in the literature (Ward, 1969; Stock *et al*, 1979; Monteiro *et al*, 1993). At a given w/c ratio;

- With variation in cement and water contents, changes in flexural strength were relatively minor. Cement (and, therefore, water) reduction with the inclusion of filler resulted in slightly higher flexural strengths compared to the Reference Mix (M1). The highest flexural strengths were obtained for the lowest cement and water contents (Mix M3*f*) and this effect was most notable at lower w/c ratios. At w/c ratios 0.65, 0.55 and 0.45, compared to the corresponding Reference Mixes, Mix M3*f* resulted in 8, 9 and 12% increase in flexural strengths, respectively. In general, when the fines content in the mix was allowed to deplete with cement and water reduction, *i.e.* filler omitted (M2, M3), flexural strength values tended to be similar to those of the Reference Mixes (M1).
- Raising workability through the use of superplasticizer (M4) had no clear influence on the flexural strength compared to the Reference Mix (M1). However, increasing cement and water contents (M5) resulted in a slight reduction in flexural strength up to 7%, which was greatest at w/c ratio 0.65.

28-day flexural / compressive strength ratio was lowest at the lowest w/c ratio for all concrete mixes, as expected, reflecting highest compressive strength at the lowest w/c ratio. In general, for a given w/c ratio, reducing cement content slightly reduced the flexural / compressive strength ratio, suggesting there was a tendency for increased brittleness.

Table 4.4 Flexural strength of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	FLEXURAL STRENGTH		
		N/mm^2	% of M1	Flexural strength / Compressive strength
	M5*	3.8	93	0.113
	M4*#	4.0	98	0.111
	M1	4.1	100	0.121
0.65	M2*f*#	4.2	102	0.118
	M2#	4.1	100	0.124
	M3*f*#	4.3	105	0.115
	M3#	4.0	98	0.116
	M5*	4.3	96	0.108
	M4*#	4.5	100	0.107
	M1	4.5	100	0.114
0.55	M2*f*#	4.6	102	0.111
	M2#	4.5	100	0.113
	M3*f*#	4.9	109	0.111
	M3#	4.4	98	0.107
	M5*	4.6	94	0.091
	M4*#	n/t	n/t	n/t
	M1	4.9	100	0.097
0.45	M2*f*#	n/t	n/t	n/t
	M2#	n/t	n/t	n/t
	M3*f*#	5.5	112	0.099
	M3#	5.2	106	0.101

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

Increasing flexural strength with reducing w/c ratio is due to improved quality of the cement paste and hence improved bond strength between the cement paste and aggregate. However, in line with previous studies (Raphael, 1984; Oluokun, 1991), reducing 28-day flexural / compressive strength ratio with reducing w/c ratio and slight concave downward curvature of the relationship between flexural and compressive strengths (see Figure 4.4 (c)), demonstrate that flexural strength does not increase as fast as compressive strength.

When the relationship between cement content and flexural strength is considered, it may be expected that flexural strength will increase with cement and water reduction in equal proportion, reflecting the effects for compressive strength. However, the results indicate that these beneficial effects are likely to be diminished by influences of the ITZ, as discussed earlier, and reduced

binding to the increased quantity of aggregate particles due to reduced paste. In addition, the beneficial effect on compressive strength due to physical contact between increased aggregate particles may not apply for flexural strength. With the inclusion of limestone filler, flexural strength increased slightly, probably due to increasing paste quantity and quality, which overshadows the effect of ITZ.

4.3.3 Static Modulus of Elasticity

Table 4.5 gives the static modulus of elasticity results. In the main, they agree with two previous studies given in literature review (Stock *et al*, 1979; Monteiro *et al*, 1993). At w/c ratio 0.55;

- The effect on modulus of variation in cement and water contents was generally in agreement with the trends noted for compressive strength, *i.e.* higher modulus at lower cement and water contents, particularly where the filler was used to maintain the fines content. As expected, Mix M3*f* resulted in the highest modulus value (9% increase) compared to the Reference Mix (M1).
- Raising workability from 75 to 180 mm nominal slump with the use of superplasticizer (M4) resulted in a slight increase in modulus of elasticity compared to the Reference Mix (M1), however, increasing cement and water contents (M5) resulted in a slight reduction.
- Whilst both elastic modulus and 28-day cube strength were influenced by variation in cement and water contents, generally, at a given strength, the modulus remained above the lower limit (and below the upper limit) given in Part 2 of BS 8110 (BSI, 1985).

Table 4.5 Static modulus of elasticity of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	STATIC MODULUS OF ELASTICITY	
		kN/mm^2	% of M1
0.55	M5*	22.0	96
	M4*#	24.0	104
	M1	23.0	100
	M2*f*#	24.0	104
	M2#	23.5	102
	M3*f*#	25.0	109
	M3#	23.5	102

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

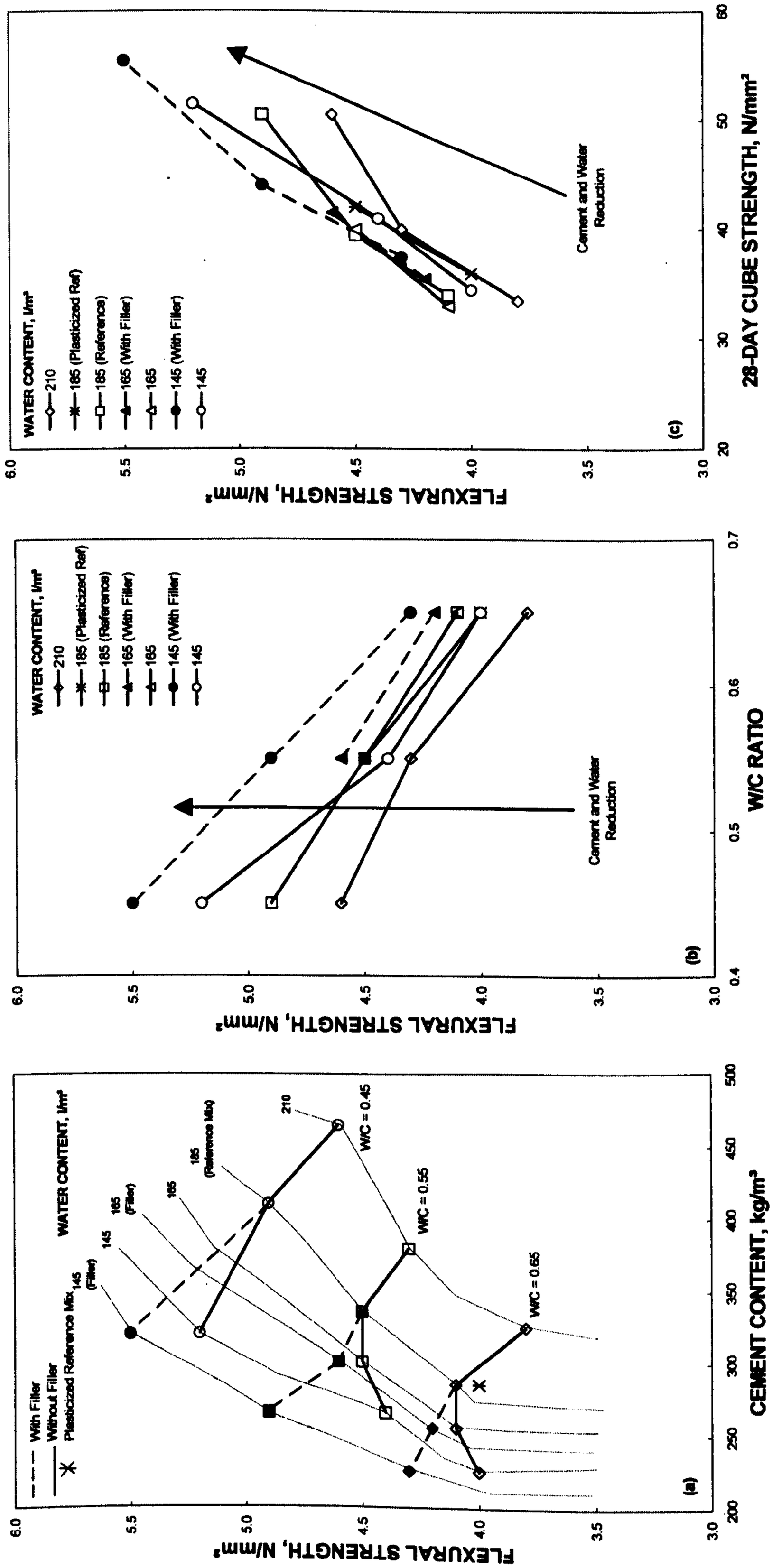


Figure 4.4 Effect of cement content on flexural strength of concrete made with dokomitic magnesium limestone coarse aggregate

In general, aggregate, which has a higher modulus of elasticity compared to the cement paste, provides restraint to the deformation and cement paste undergoes elastic deformation (Neville, 1995). Therefore, cement-and-water-reduced concrete at fixed w/c ratio (with increased aggregate content and reduced cement paste) is likely to result in higher elastic modulus values. However, these beneficial effects may be partly offset by negative effects due to increasing ITZ. For example, a 20 l/m^3 water (and cement) reduction (M2) increased modulus of elasticity by 0.5 KN/mm^2 compared to the Reference Mix (M1), but a further 20 l/m^3 water reduction (M3) had no further effect. The mixes with limestone filler resulted in an even greater increase in modulus of elasticity, possibly due to mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, chemical reactivity and absorption / adsorption characteristics of limestone filler. In addition, it should be noted that an increase in compressive strength is also likely to have a positive effect on modulus of elasticity, as the variation in cement content at fixed w/c ratio 0.55 had similar influence on both of these properties (see Tables 4.3 and 4.5).

4.3.4 Load to Failure

The maximum stresses and corresponding strains determined from specimens loaded to failure are given in Tables 4.6 (a) and (b), respectively. The stress / strain relationships are shown in Figure 4.5. The results are generally in agreement with the compressive strength and modulus of elasticity results observed with variation in cement and water contents in equal proportion. At w/c ratio 0.55;

- The Reference Mix (M1) resulted in a maximum stress of 30.1 N/mm^2 and corresponding strain of 3 x 10^{-3}. Reduction in cement and water contents gave slightly higher maximum stresses and lower corresponding strains, reflecting the slightly higher stiffness obtained by concrete with higher aggregate contents and compressive strengths. As expected, this effect was most notable when the filler was included to maintain the fines content (Mix M3*f*), which resulted in a 12% increase in maximum stress and 17% decrease in corresponding strain compared to the Reference Mix (M1).
- Increasing cement (hence water) content with workability increase from 75 to 180 mm nominal slump (M5), had only a minor influence on the stress / strain characteristics of concrete in comparison to the Reference Mix (M1).

If the testing machine allows a reduction in the applied load after maximum load, allowing strain to increase at a constant rate, the complete stress / strain curve of normal weight concrete is symmetrical (to a certain extent) about a vertical axis, which goes through the maximum stress value (Neville, 1995). As the test method followed this procedure, stress / strain relationships shown in Figure 4.5, seem to be acceptable. The maximum stress values given in Table 4.6 (a), generally agree with the 28-day, 100 mm cube strengths given in Table 4.3, although the former

values are approximately 25% lower than the latter. This is due to the effect of specimen shape on strength (Neville, 1995). In addition, Figure 4.5 generally supports the modulus of elasticity values discussed earlier. In other words, it indicates that stronger concrete, particularly Mix M3*f*, exhibits a lower strain at a given stress. Therefore, it appears that the mechanisms discussed for the compressive strength and the modulus of elasticity, in relation to cement and water reduction, are also reflected in the stress / strain relationship of concrete to failure.

In addition, Figure 4.5 backs up the observation that reducing cement and water contents in equal proportion leads to increased brittleness of concrete, (*c.f.* flexural strength) indicated by steeper descending part of the stress / strain curve (Neville, 1995). However, it should be noted that this behaviour was only observed when limestone filler was included to maintain the fines content (Mix M3*f*). Overall, it appears that increased compressive strength, modulus of elasticity and more brittle behaviour of cement-and-water-reduced concrete, particularly when filler is included, are all inter-related.

Table 4.6 Load to failure of concrete made with dolomitic magnesium limestone coarse aggregate

(a) Maximum stress

W/C RATIO	MIX	MAXIMUM STRESS (σ_{max})	
		N/mm^2	% of M1
0.55	M5*	29.5	98
	M1	30.1	100
	M3*f*$^{\#}$	33.7	112
	M3$^{\#}$	32.0	106

(b) Strain at maximum stress

W/C RATIO	MIX	STRAIN AT MAXIMUM STRESS (ε, σ_{max})	
		x 10^{-3}	% of M1
0.55	M5*	2.9	97
	M1	3.0	100
	M3*f*$^{\#}$	2.5	83
	M3$^{\#}$	2.8	93

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
$^{\#}$ Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

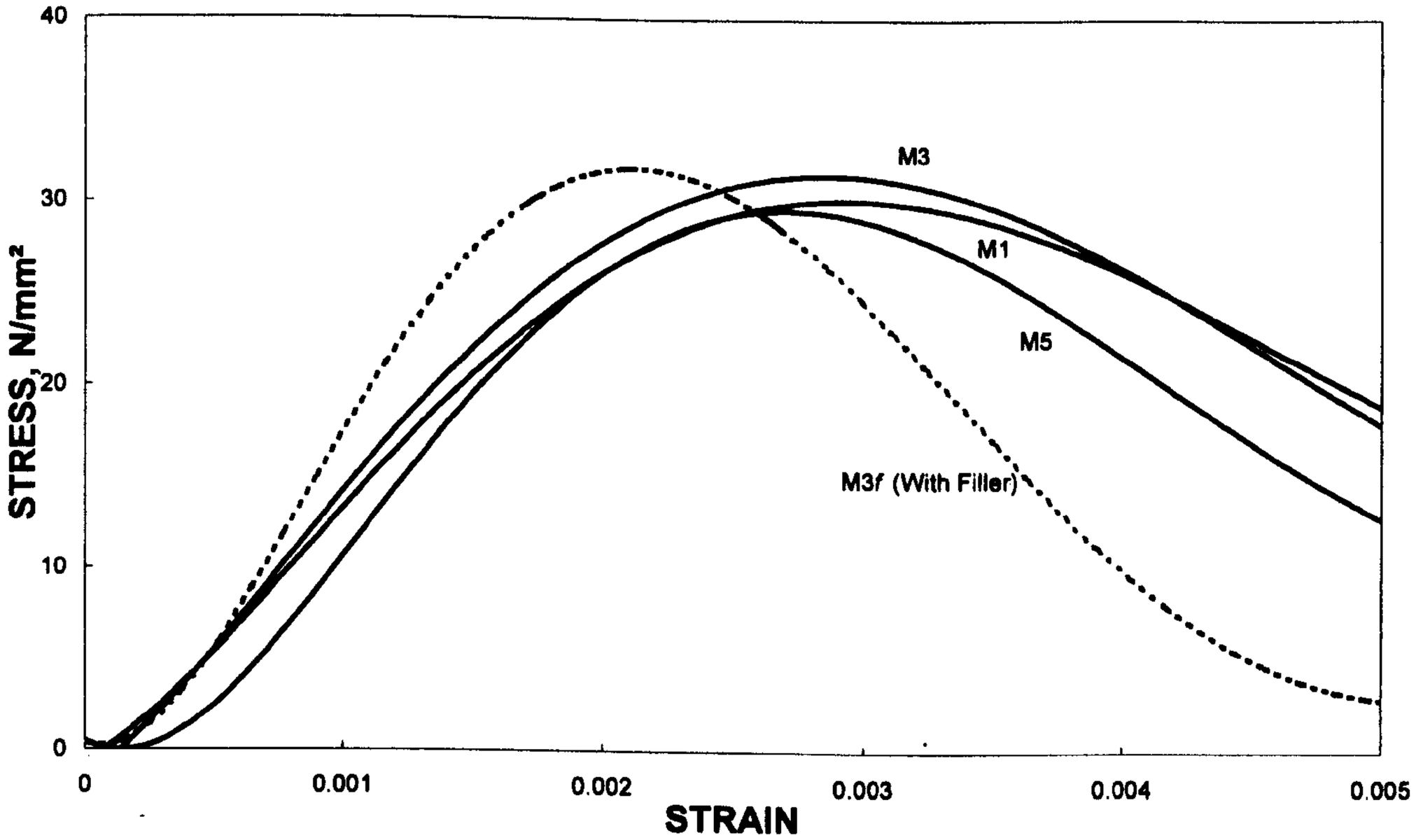


Figure 4.5 Stress / strain relationship (until failure) of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.55

4.3.5 Drying Shrinkage

The drying shrinkage measurements at 20 weeks and shrinkage plotted against drying time up to 20 weeks, are given in Table 4.7 and Figure 4.6, respectively. At w/c ratio 0.55;

- Reduction in cement and water contents reduced drying shrinkage. This effect tended to be slightly greater for mixes where the filler was used to maintain the fines content, *e.g.* Mix M3*f* resulted in the lowest shrinkage at 20 weeks and was 17% lower than that of the Reference Mix (M1).
- Raising workability from 75 to 180 mm nominal slump with the use of superplasticizer (M4) led to a higher shrinkage (12% increase compared to the Reference Mix (M1)). When cement (thus, water) content was increased, with increased workability from 75 to 180 mm nominal slump (M5), shrinkage increased by 29% compared to the Reference Mix (M1).

The reduction in drying shrinkage with cement and water reduction at fixed w/c ratio is in line with previous studies presented in the literature review (Shoya, 1979; Hansen and Almudaiheem, 1987; Bissonnette *et al*, 1999). This is due to reduced quantity of cement paste that undergoes shrinkage and increased volume of aggregate that acts as a restraint. Indeed, Bissonnette *et al* (1999) have shown that shrinkage is directly proportional to the volume of cement paste. Furthermore, due to reduced paste content and increased aggregate content, there is likely to be greater point-to-point contact between aggregate particles, allowing less opportunity for shrinkage.

Table 4.7 Drying shrinkage of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	DRYING SHRINKAGE^{S} (20 WEEKS)	
		x 10^{-6}	% of M1
0.55	M5*	701	129
	M4*#	607	112
	M1	542	100
	M2*f*#	517	95
	M2#	538	99
	M3*f*#	450	83
	M3#	475	88

^{S} *Drying at 20°C, 55% RH*
All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

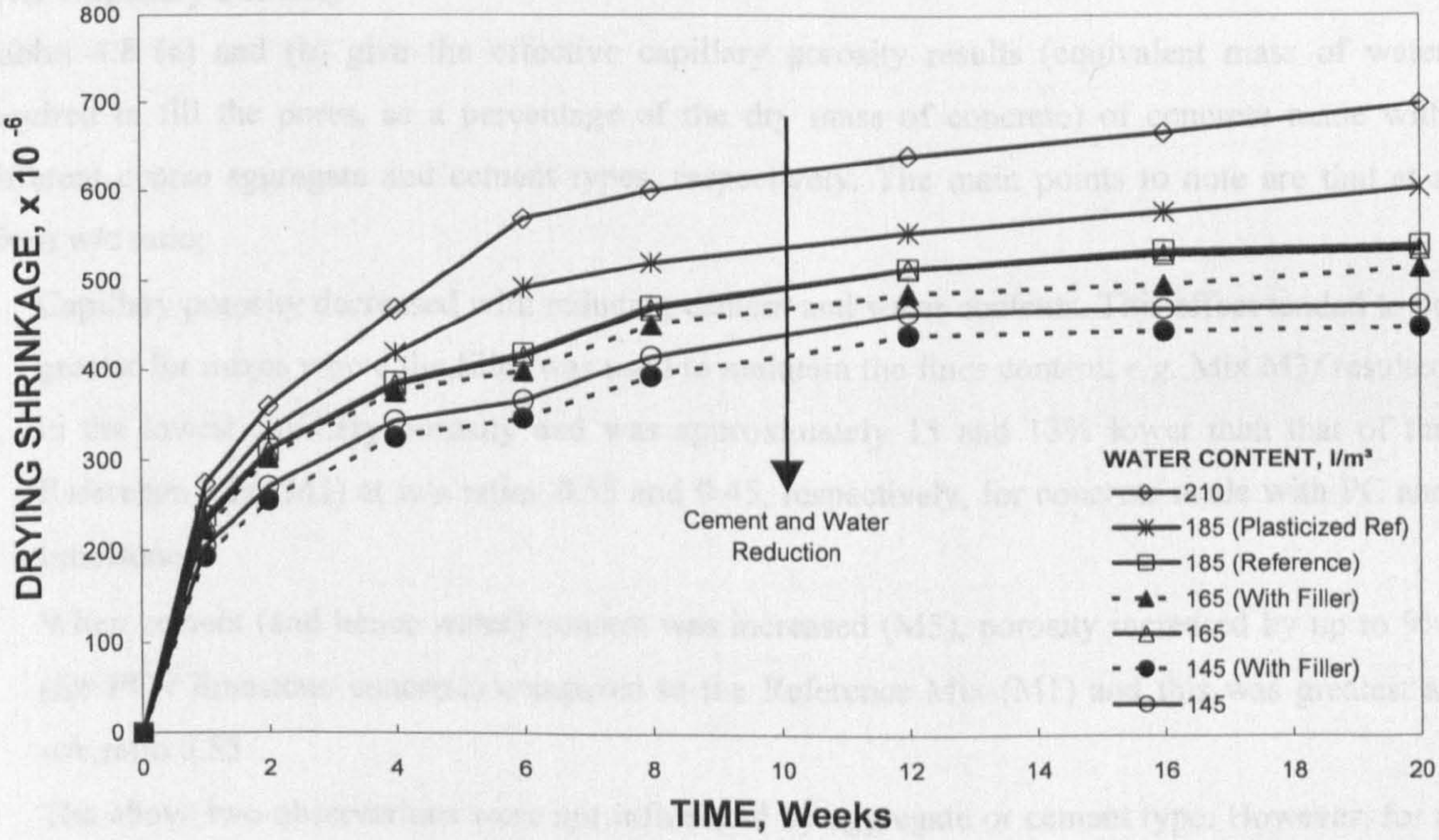


Figure 4.6 Drying shrinkage of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.55

Further reduction in shrinkage of mixes with limestone filler is probably due to the possible reduction in free water due to absorbing / adsorbing characteristics of the filler and reduced bleeding, which reduces the number of bleed channels (routes for moisture loss). On the other hand, it should be noted that mixes with filler increased the fines content by reducing sand content, while the coarse aggregate content remained equal to that of the corresponding mixes without filler.

Therefore, mixes made with-or-without filler should have similar restraining effects to shrinkage. Slightly increased shrinkage when superplasticizer was added to raise workability from 75 to 180 mm nominal slump (M4), may be due to less coarse aggregate content in the mix (less restrain to the shrinkage) compared to that in the Reference Mix (M1).

4.4 PERMEATION PROPERTIES

Capillary porosity (which is not a permeation property, but higher porosity with interconnected pores contributes to enhance the transport of fluids through concrete), water absorption and ISA tests were carried out on concrete made with a range of cement and coarse aggregate types, which was used for the reinforcement corrosion study. Five concrete mixes (M5, M1, M2*f*, M2 and M3*f*) were selected at w/c ratios 0.55 and 0.45 for PC / limestone concrete. Only three mixes (M5, M1 and M3*f*) made at w/c ratios 0.55 and 0.45 were used for all other cement / aggregate combinations. In addition, both ISA and air permeability tests were carried out for PC / limestone concrete (all seven mixes) made at w/c ratios 0.65, 0.55 and 0.45, as a part of Stage 1, mentioned in Chapter 3.

4.4.1 Capillary Porosity

Tables 4.8 (a) and (b) give the effective capillary porosity results (equivalent mass of water required to fill the pores, as a percentage of the dry mass of concrete) of concrete made with different coarse aggregate and cement types, respectively. The main points to note are that at a given w/c ratio;

- Capillary porosity decreased with reducing cement and water contents. This effect tended to be greater for mixes where the filler was used to maintain the fines content, *e.g.* Mix M3*f* resulted in the lowest capillary porosity and was approximately 15 and 13% lower than that of the Reference Mix (M1) at w/c ratios 0.55 and 0.45, respectively, for concrete made with PC and limestone.
- When cement (and hence water) content was increased (M5), porosity increased by up to 9% (for PC / limestone concrete) compared to the Reference Mix (M1) and this was greatest at w/c ratio 0.55.
- The above two observations were not influenced by aggregate or cement type. However, for a given mix, capillary porosity increased with increasing water absorption of aggregates. Concrete made with PC / limestone (aggregate with the highest absorption) resulted in an increase in porosity (approximately from 60 to 88%) for equivalent mixes compared to concrete made with PC / granite (aggregate with the lowest absorption).
- Porosity values of PC / PFA and PC / GGBS concrete were up to 9 and 17% lower than equivalent mixes made with PC, 42.5 N, respectively, and this effect was greatest at w/c ratio 0.55.

Table 4.8 Effective capillary porosity of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	CAPILLARY POROSITY					
		Water to fill pores % by dry mass of concrete			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
0.55	M5*	6.1	5.0	8.2	105	106	109
	M1	5.8	4.7	7.5	100	100	100
	M2*f*#	n/t	n/t	7.1	n/t	n/t	95
	M2#	n/t	n/t	7.4	n/t	n/t	99
	M3*f*#	4.2	3.8	6.4	72	81	85
0.45	M5*	5.1	4.3	7.3	102	102	103
	M1	5.0	4.2	7.1	100	100	100
	M2*f*#	n/t	n/t	6.6	n/t	n/t	93
	M2#	n/t	n/t	6.9	n/t	n/t	97
	M3*f*#	4.1	3.3	6.2	82	79	87

(b) Made with different cement types

W/C RATIO	MIX	CAPILLARY POROSITY					
		Water to fill pores % by dry mass of concrete			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
0.55	M5*	8.2	7.6	6.8	109	107	103
	M1	7.5	7.1	6.6	100	100	100
	M2*f*#	7.1	n/t	n/t	95	n/t	n/t
	M2#	7.4	n/t	n/t	99	n/t	n/t
	M3*f*#	6.4	5.8	5.7	85	82	86
0.45	M5*	7.3	6.9	6.6	103	105	102
	M1	7.1	6.6	6.5	100	100	100
	M2*f*#	6.6	n/t	n/t	93	n/t	n/t
	M2#	6.9	n/t	n/t	97	n/t	n/t
	M3*f*#	6.2	5.7	5.6	87	86	86

All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

Porosity represents the proportion of the total volume of concrete occupied by pores, whilst capillary porosity measures the amount of voids occupied by capillary pores, and permeation properties of hardened cement paste are mainly governed by its capillary porosity (Neville, 1995).

As expected, capillary porosity reduced with reducing w/c ratio from 0.55 to 0.45. To explain this, it should be noted that for full hydration to be achieved, a w/c ratio of approximately 0.25 is required and, thus, w/c ratios above this result in excess water compared to the quantity of cement available for hydration (Dhir and Jackson, 1996). This excess water leads to voids in the hardened concrete (either filled with water or air, depending on the moisture condition of concrete).

Zhou (2001) suggests that reduction in cement and water contents in equal proportion reduces the porosity of concrete due to reduced cement paste (higher porosity component) and increased aggregate content (lower porosity component). Indeed, this explains the reduced capillary porosity of concrete with cement (and hence water) reduction at fixed w/c ratio.

Reduction in capillary porosity of concrete with reducing cement and water contents in equal proportion agrees with compressive strength results given in Section 4.3.1. However, as discussed for compressive strength, it should be noted that increased aggregate content increases the effective ITZ area, which has the highest porosity of the composite (Winslow *et al*, 1994). On the other hand, reduced bleeding, with cement and water reduction, tends to eliminate (partly or completely) collecting bleed water below the aggregates and developing bleed channels, which create porous weak zones of higher w/c ratio.

Inclusion of limestone filler further reduces capillary porosity with improved quality of the cement paste, possibly due to mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, chemical reactivity and absorption / adsorption characteristics of limestone filler.

The similar variation in capillary porosity values with cement and water contents at fixed w/c ratio for concrete made with different coarse aggregates, validates the above discussion. However, it is to be noted that the effect of aggregate type was more pronounced than the variation in cement and water contents in equal proportion. This is likely to be due to the variations in porosity of the aggregates. As mentioned earlier, cement paste may be absorbed into the open pores of aggregates with higher porosity (Zhang and Gjorv, 1990) and limestone aggregate may react with PC hydration products (Monteiro and Metha, 1986; Tasang *et al*, 1998). Both of these may lead to improve the interface between aggregates and cement paste, reducing porosity. However, the results indicate that these effects were not dominating.

As expected, capillary porosity of concrete made with PC / PFA or PC / GGBS was lower than that of equivalent PC concrete. This is likely to be due to improved particle packing (due to increased fines content), enhanced hydration of PC particles (through greater dissemination of PC flocs by PFA or GGBS) and pozzolanic properties, which produce a denser microstructure (Mehta, 1980; Roy and Idorn, 1983; Dhir, 1986). In addition, improved particle packing of concrete containing PFA or GGBS restricts free water movements or bleeding to the upper surface, eliminating porous weak zones of higher w/c ratio.

4.4.2 Water Absorption

The water absorption results (percentage of dry mass of concrete) of concrete made with different coarse aggregate and cement types are given in Tables 4.9 (a) and (b), respectively. They are generally in line with previous studies presented in the literature review (Keene, 1960; Buenfeld and Okundi, 1998). At a given w/c ratio;

- The changes occurring with cement and water reduction were essentially similar to those noted for capillary porosity. The greatest reduction in water absorption was observed for Mix M3*f* and 24-hour water absorption was approximately 34% lower (at both w/c ratios 0.55 and 0.45) than that of the Reference Mix (M1) for concrete made with PC and limestone.
- When cement (and hence water) content was increased (M5), water absorption slightly increased (approximately 6% for PC / limestone concrete, at both w/c ratios) compared to the Reference Mix (M1).
- The above observations with variation in cement and water contents were essentially similar for concrete made with different aggregate and cement types. As expected, for a given mix, water absorption of concrete increased with increasing water absorption of aggregates. This was as high as approximately 50% (for some mixes) for concrete made with PC / limestone compared to equivalent mixes made with PC / granite. In addition, the effect of cement reduction was more pronounced for concrete made with PC / limestone compared to that made with PC and other aggregate types.
- The use of PC / PFA or PC / GGBS resulted in lower water absorptions, which were up to 22 and 24% lower than that of equivalent mixes (at w/c ratio 0.45) made with PC, 42.5 N, respectively. In addition, the effect of cement reduction was more pronounced for concrete made with PC compared to that made with PC / PFA or PC / GGBS.

Porosity may provide an indication of absorption. However, high porosity does not necessarily imply higher water absorption because pores may be discontinuous or ineffective with respect to transport (Neville, 1995). However, the mechanisms discussed for capillary porosity may also influence water absorption. In addition, increased aggregate content in cement-and-water-reduced mixes is likely to provide greater restrictions to capillary suction by discontinuity of the capillary

pores and greater tortuosity of the flow paths, reducing absorption (McCarter *et al*, 1992). Furthermore, reduced shrinkage with cement and water reduction may lead to less microcracks in ITZ and, consequently, to reduced absorption (Neville, 1995).

Table 4.9 Water absorption of concrete

(a) Made with different coarse aggregate types

W/C RATIO	COARSE AGGREGATE	MIX	WATER ABSORPTION					
			% of dry mass of concrete			% of M1		
			30 Min	60 Min	24 Hrs	30 Min	60 Min	24 Hrs
0.55	Natural Gravel	M5*	0.50	0.67	3.6	106	105	106
		M1	0.47	0.64	3.4	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.41	0.55	2.7	87	86	79
	Granite	M5*	0.48	0.64	3.4	107	107	106
		M1	0.45	0.60	3.2	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.39	0.52	2.5	87	87	78
	Limestone	M5*	0.68	1.01	4.5	105	106	105
		M1	0.65	0.95	4.3	100	100	100
		M2*f*#	0.57	0.77	3.1	88	81	72
		M2#	0.59	0.79	3.2	91	83	74
		M3*f*#	0.50	0.71	2.9	77	75	67
0.45	Natural Gravel	M5*	0.44	0.55	3.0	110	106	107
		M1	0.40	0.52	2.8	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.32	0.41	2.1	80	79	75
	Granite	M5*	0.41	0.54	2.9	108	108	107
		M1	0.38	0.50	2.7	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.31	0.40	2.0	82	80	74
	Limestone	M5*	0.65	0.97	4.3	105	107	105
		M1	0.62	0.91	4.1	100	100	100
		M2*f*#	0.53	0.72	2.9	85	79	71
		M2#	0.55	0.74	3.0	89	81	73
		M3*f*#	0.47	0.66	2.7	76	73	66

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

Table 4.9 Water absorption of concrete

(b) Made with different cement types

W/C RATIO	CEMENT	MIX	WATER ABSORPTION					
			% of dry mass of concrete			% of M1		
			30 Min	60 Min	24 Hrs	30 Min	60 Min	24 Hrs
0.55	PC, 42.5 N	M5*	0.68	1.01	4.5	105	106	105
		M1	0.65	0.95	4.3	100	100	100
		M2*f*#	0.57	0.77	3.1	88	81	72
		M2#	0.59	0.79	3.2	91	83	74
		M3*f*#	0.50	0.71	2.9	77	75	67
	PC / PFA	M5*	0.58	0.88	4.1	107	107	111
		M1	0.54	0.82	3.7	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.48	0.68	2.8	89	83	76
	PC / GGBS	M5*	0.55	0.85	4.0	104	106	111
		M1	0.53	0.80	3.6	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.43	0.65	2.7	81	81	75
0.45	PC, 42.5 N	M5*	0.65	0.97	4.3	105	107	105
		M1	0.62	0.91	4.1	100	100	100
		M2*f*#	0.53	0.72	2.9	85	79	71
		M2#	0.55	0.74	3.0	89	81	73
		M3*f*#	0.47	0.66	2.7	76	73	66
	PC / PFA	M5*	0.55	0.78	3.6	117	110	113
		M1	0.47	0.71	3.2	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.41	0.58	2.4	87	82	75
	PC / GGBS	M5*	0.42	0.65	3.5	105	105	113
		M1	0.40	0.62	3.1	100	100	100
		M2*f*#	n/t	n/t	n/t	n/t	n/t	n/t
		M2#	n/t	n/t	n/t	n/t	n/t	n/t
		M3*f*#	0.34	0.51	2.3	85	82	74

All mixes contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

4.4.3 Initial Surface Absorption (ISA)

Table 4.10 gives the ISA-10 data obtained for concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate. The results are plotted in Figures 4.7 (a) to (c) against cement content, w/c ratio and 28-day cube strength, respectively. For a given w/c ratio;

- ISA-10 progressively reduced with cement and water reduction and was least for mixes having filler to maintain the fines content equal to that of the Reference Mix (M1). Thus, Mix M3*f* (with filler) resulted in the lowest ISA-10, which was typically 26% lower (at all w/c ratios) in comparison to the Reference Mix (M1).
- ISA-10 reduced slightly (approximately 3% compared to the Reference Mix (M1) at all w/c ratios) when superplasticizer was used to raise workability from 75 to 180 mm nominal slump (M4). When cement (thus, water) content was increased (M5), ISA-10 increased by 18 to 34% compared to the Reference Mix (M1) and this effect was most notable at lower w/c ratios.

Comparison of the ISA-10 of concrete made with different coarse aggregate and cement types is shown in Tables 4.11 (a) and (b), respectively. It indicates that at a given w/c ratio;

- The effect of variation in cement and water contents on ISA-10 was not influenced by aggregate or cement type. As for other permeation properties, for a given mix, ISA-10 of concrete increased with increasing water absorption of aggregates. This was approximately 25 to 52% higher for concrete made with PC / limestone compared to equivalent mixes made with PC / granite. In addition, when cement and water contents were increased (M5), PC / limestone concrete showed a more pronounced increase in ISA-10 compared to concrete made with PC and other aggregate types.
- As for other permeation properties, ISA-10 values of PC / PFA and PC / GGBS concrete were up to 6 and 9% lower (at both w/c ratios) than equivalent mixes made with PC, 42.5 N, respectively.

ISA-10 results agree with previous studies presented in the literature review (Dhir *et al*, 1987a; Dhir *et al*, 1987b; Dhir *et al*, 1996; McCarthy *et al*, 1996). The observed behaviour is likely to be due to mechanisms (combined or individual action) discussed in the capillary porosity and water absorption sections. Slightly reduced ISA-10 when superplasticizer was used to raise workability from 75 to 180 mm nominal slump (Mix M4, which was not used for the capillary porosity and water absorption tests), may be due to improved microstructure through better deflocculation and dispersion of cement particles and, consequently, better hydration. However, Dhir *et al* (1987b) suggest that this effect on ISA is minor.

Table 4.10 Initial surface absorption of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	INITIAL SURFACE ABSORPTION (ISA–10)	
		ml/m^2/s	% of M1
0.65	M5*	0.78	118
	M4*$^{\#}$	0.64	97
	M1	0.66	100
	M2*f*$^{\#}$	0.52	79
	M2$^{\#}$	0.54	82
	M3*f*$^{\#}$	0.49	74
	M3$^{\#}$	0.51	77
0.55	M5*	0.71	125
	M4*$^{\#}$	0.55	96
	M1	0.57	100
	M2*f*$^{\#}$	0.45	79
	M2$^{\#}$	0.46	81
	M3*f*$^{\#}$	0.42	74
	M3$^{\#}$	0.43	75
0.45	M5*	0.67	134
	M4*$^{\#}$	0.49	98
	M1	0.50	100
	M2*f*$^{\#}$	0.38	76
	M2$^{\#}$	0.39	78
	M3*f*$^{\#}$	0.37	74
	M3$^{\#}$	0.38	76

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
$^{\#}$ Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

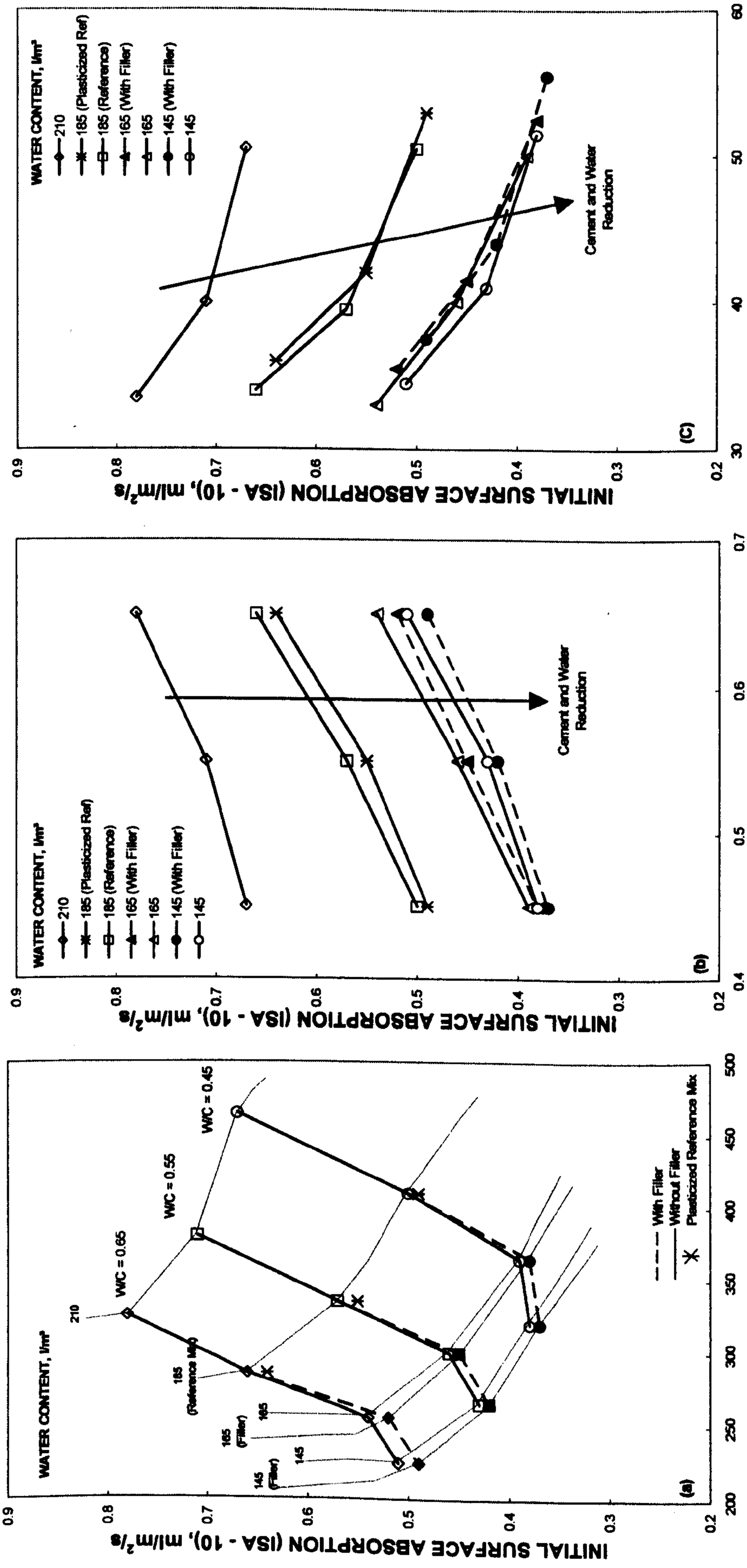


Figure 4.7 Effect of cement content on initial surface absorption of concrete made with dolomitic magnesium limestone coarse aggregate

Table 4.11 Initial surface absorption of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	INITIAL SURFACE ABSORPTION (ISA–10)					
		ml/m²/s			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
0.55	M5*	0.58	0.50	0.71	109	111	125
	M1	0.53	0.45	0.57	100	100	100
	M2*f*#	n/t	n/t	0.45	n/t	n/t	79
	M2#	n/t	n/t	0.46	n/t	n/t	81
	M3*f*#	0.41	0.33	0.42	77	73	74
0.45	M5*	0.48	0.44	0.67	107	110	134
	M1	0.45	0.40	0.50	100	100	100
	M2*f*#	n/t	n/t	0.38	n/t	n/t	76
	M2#	n/t	n/t	0.39	n/t	n/t	78
	M3*f*#	0.34	0.26	0.37	76	65	74

(b) Made with different cement types

W/C RATIO	MIX	INITIAL SURFACE ABSORPTION (ISA–10)					
		ml/m²/s			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
0.55	M5*	0.71	0.67	0.66	125	124	127
	M1	0.57	0.54	0.52	100	100	100
	M2*f*#	0.45	n/t	n/t	79	n/t	n/t
	M2#	0.46	n/t	n/t	81	n/t	n/t
	M3*f*#	0.42	0.40	0.39	74	74	75
0.45	M5*	0.67	0.63	0.62	134	129	129
	M1	0.50	0.49	0.48	100	100	100
	M2*f*#	0.38	n/t	n/t	76	n/t	n/t
	M2#	0.39	n/t	n/t	78	n/t	n/t
	M3*f*#	0.37	0.36	0.35	74	73	73

All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

4.4.4 Air Permeability

Given that the trends seen with the ISA test were very similar to the air permeability results, air permeability test was limited only to PC / limestone concrete. The air permeability results of concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate are given in

Table 4.12 and plotted in Figures 4.8 (a) to (c) against cement content, w/c ratio and 28-day cube strength, respectively. They are generally in line with previous studies given in the literature review (Mills, 1987; Basheer *et al*, 1994; Buenfeld and Okundi, 1998). For a given w/c ratio;

- The changes occurring with cement and water reduction were essentially similar to those noted for ISA-10, *e.g.* Mix M3*f* resulted in the highest reduction in air permeability of approximately 45% (at all w/c ratios) compared to the Reference Mix (M1).
- Raising workability from 75 to 180 mm nominal slump using superplasticizer (M4) had only a minor influence on air permeability in comparison to the Reference Mix (M1) with slight reductions of approximately 6% at all w/c ratios. When cement and water contents were increased (M5), however, air permeability increased by typically 13% (at all w/c ratios) in comparison to the Reference Mix (M1).

Table 4.12 Intrinsic air permeability of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	INTRINSIC AIR PERMIABILITY	
		$m^2 \times 10^{-17}$	% of M1
0.65	M5*	12.6	113
	M4*#	10.5	94
	M1	11.2	100
	M2*f*#	8.6	77
	M2#	9.5	85
	M3*f*#	6.4	57
	M3#	7.6	68
0.55	M5*	10.6	114
	M4*#	8.7	94
	M1	9.3	100
	M2*f*#	6.8	73
	M2#	8.0	86
	M3*f*#	5.2	56
	M3#	6.2	67
0.45	M5*	9.5	113
	M4*#	7.8	93
	M1	8.4	100
	M2*f*#	6.3	75
	M2#	7.2	86
	M3*f*#	4.5	54
	M3#	5.7	68

All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

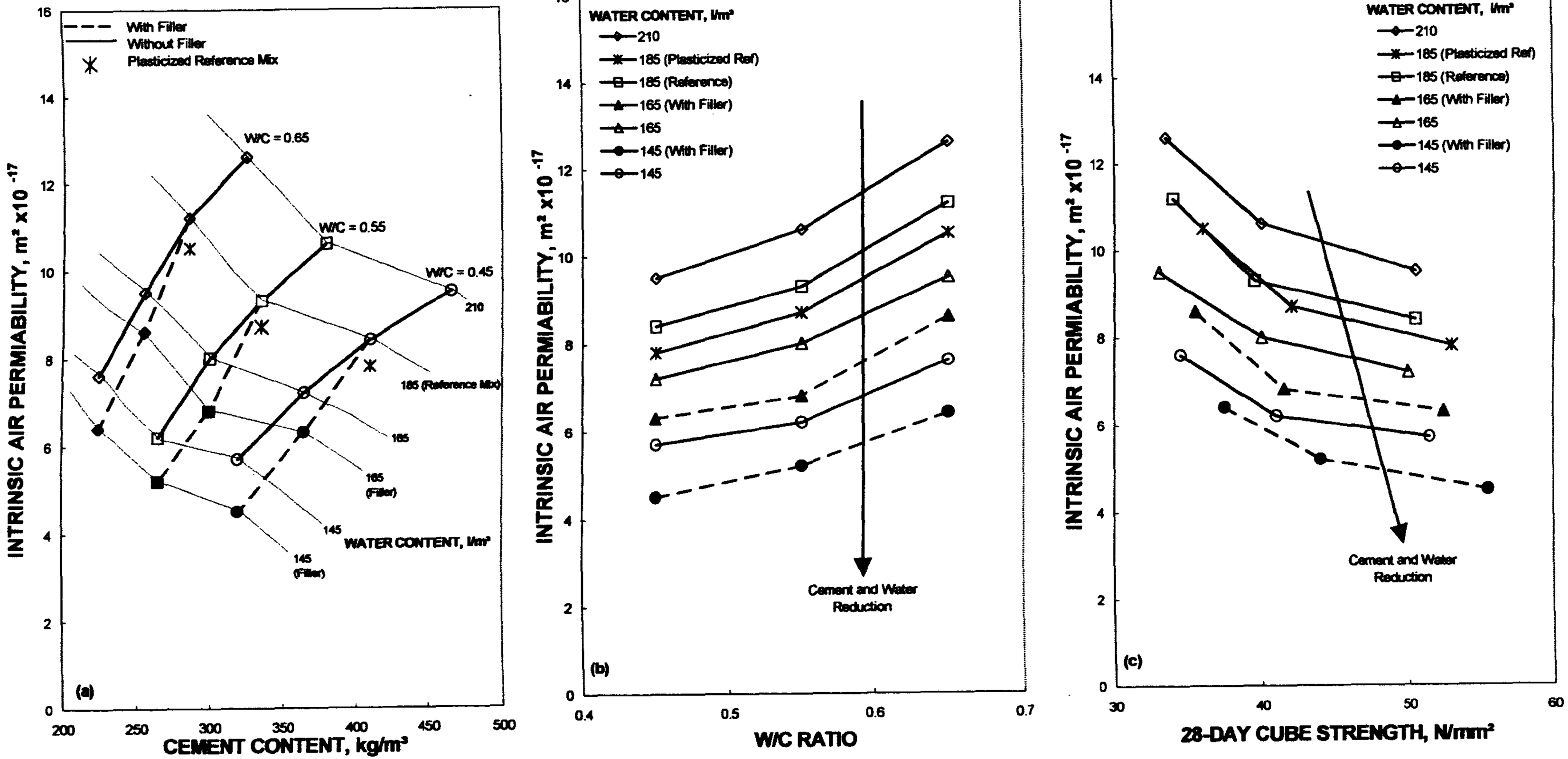


Figure 4.8 Effect of cement content on intrinsic air permeability of concrete made with dolomitic magnesium limestone coarse aggregate

Variation in air permeability with cement content at fixed w/c ratio is similar to that of capillary porosity, water absorption and ISA-10 and, therefore, mechanisms discussed above are also likely to control air permeability. The most notable variation in air permeability is its even, more pronounced reduction with cement and water reduction compared to water absorption and ISA-10.

4.5 DURABILITY PROPERTIES

A range of concrete mixes of different w/c ratios, which included those appropriate to the relevant exposure as given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate was tested for durability properties. Carbonation resistance of concrete was tested at w/c ratios 0.65 (all seven concrete mixes), 0.55 and 0.45 (Mixes M5, M1, M3*f* and M3). Chloride diffusion using the PD (potential difference) test was carried out at w/c ratios 0.65, 0.55 (Mixes M5, M1, M3*f* and M3) and 0.45 (all seven mixes). All concrete mixes at w/c ratio 0.45 were tested for sulfate resistance and freeze / thaw resistance. Abrasion depths were measured at w/c ratio 0.50 for all seven concrete mixes.

4.5.1 Carbonation Resistance

Figure 4.9 shows the carbonation depth measurements (up to 20 weeks) of concrete at w/c ratio 0.65, plotted against the square root of the exposure period, as a typical example. The carbonation depths of concrete (water-cured at 20°C to 28 days), measured after accelerated exposure (20 weeks), are given in Table 4.13 and plotted in Figures 4.10 (a) to (e) against cement content, w/c ratio, 28-day cube strength, ISA-10 and air permeability, respectively. The main points to note from the data are, at a given w/c ratio;

- When cement and water contents were reduced, carbonation depth tended to be slightly higher than that of the Reference Mix (M1). This effect was most notable when the fines content was allowed to deplete and, therefore, Mix M3 resulted in the highest carbonation depth compared to the Reference Mix (M1). The highest increase (18%) was observed at w/c ratio 0.65. However, this was partly offset with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix (M1).
- When workability was raised from 75 to 180 mm nominal slump through the use of superplasticizer (M4 tested only at w/c ratio 0.65) and when cement and water contents were increased (M5, at all w/c ratios), carbonation depth reduced slightly up to 2.5 and 1.0 mm, respectively, compared to the Reference Mix (M1).

Table 4.13 Carbonation resistance of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	CARBONATION DEPTH[$] (20 WEEKS)	
		mm	% of M1
0.65	M5*	27.5	96
	M4*[#]	26.0	91
	M1	28.5	100
	M2*f*[#]	28.5	100
	M2[#]	29.0	102
	M3*f*[#]	30.5	107
	M3[#]	33.5	118
0.55	M5*	17.0	97
	M4*[#]	n/t	n/t
	M1	17.5	100
	M2*f*[#]	n/t	n/t
	M2[#]	n/t	n/t
	M3*f*[#]	18.0	103
	M3[#]	19.0	109
0.45	M5*	9.0	90
	M4*[#]	n/t	n/t
	M1	10.0	100
	M2*f*[#]	n/t	n/t
	M2[#]	n/t	n/t
	M3*f*[#]	10.5	105
	M3[#]	11.0	110

[$] *4.0% CO_2 exposure, 20°C, 55% RH*
All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] *Superplastizer added to maintain workability*
f Filler included to maintain fines content equal to that of M1
n/t Not tested

The near linear relationship between carbonation depth and square root of the exposure period, as given in Figure 4.9, is in line with generally accepted behaviour for carbonation depth variation under steady hygrometric conditions (BRE, 1995).

As expected, w/c ratio had a dominant effect on carbonation of concrete and carbonation depth (at a given time) increased with increasing w/c ratio. In addition, the results indicate that the influence of cement content on carbonation is small compared to that of the w/c ratio.

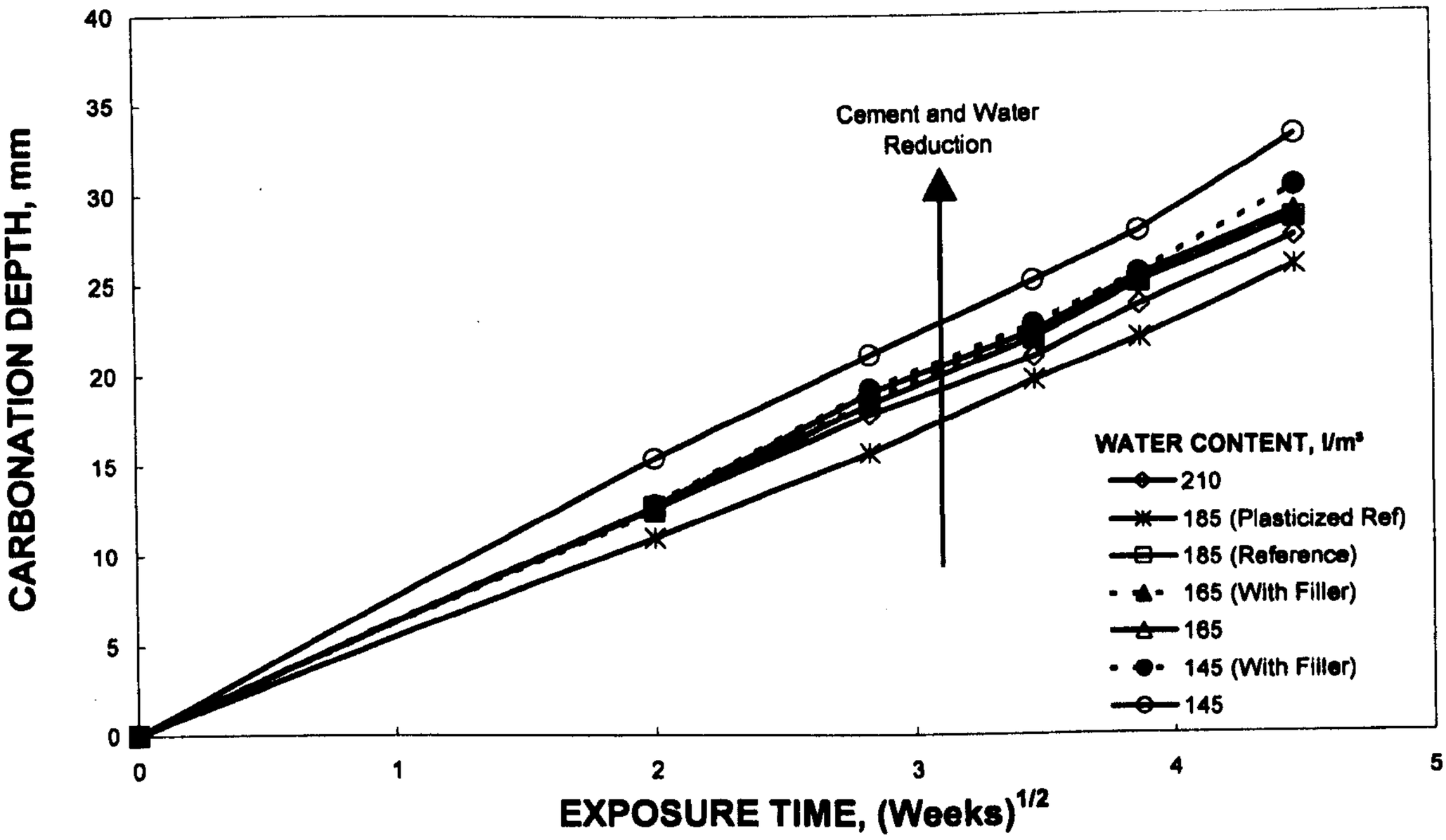


Figure 4.9 Carbonation of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.65

Before discussing the influence of variation in cement and water contents in equal proportion on carbonation resistance of concrete, it is worth comparing these results with those reviewed in the literature review, see Section 2.4.4. The literature indicates that carbonation resistance is either unchanged or improved slightly (in some cases) with cement and water reduction in equal proportion. In contrast, the results reported here, indicate that carbonation resistance is slightly decreased with cement and water reduction.

Whilst the compressive strength and air permeability (and other permeation properties as well) generally increased and decreased, respectively, with reduction in cement and water contents in equal proportion, the observed carbonation results are, perhaps, unexpected (see Figure 4.10). However, this should not be surprising since carbonation is mainly influenced by carbon dioxide diffusivity into concrete, which is not necessarily directly related to air permeability or compressive strength (Neville, 1995). Indeed, Buenfeld and Okundi (1998) showed that whilst there is a clear reduction in oxygen permeability as cement and water contents are reduced in equal proportion, the oxygen diffusion coefficient did not show similar reductions. In addition, as cement and water contents are reduced, there is a reduction in the quantity of cement paste available to react with carbon dioxide, *i.e.* for neutralisation, which may also have influenced the observed results.

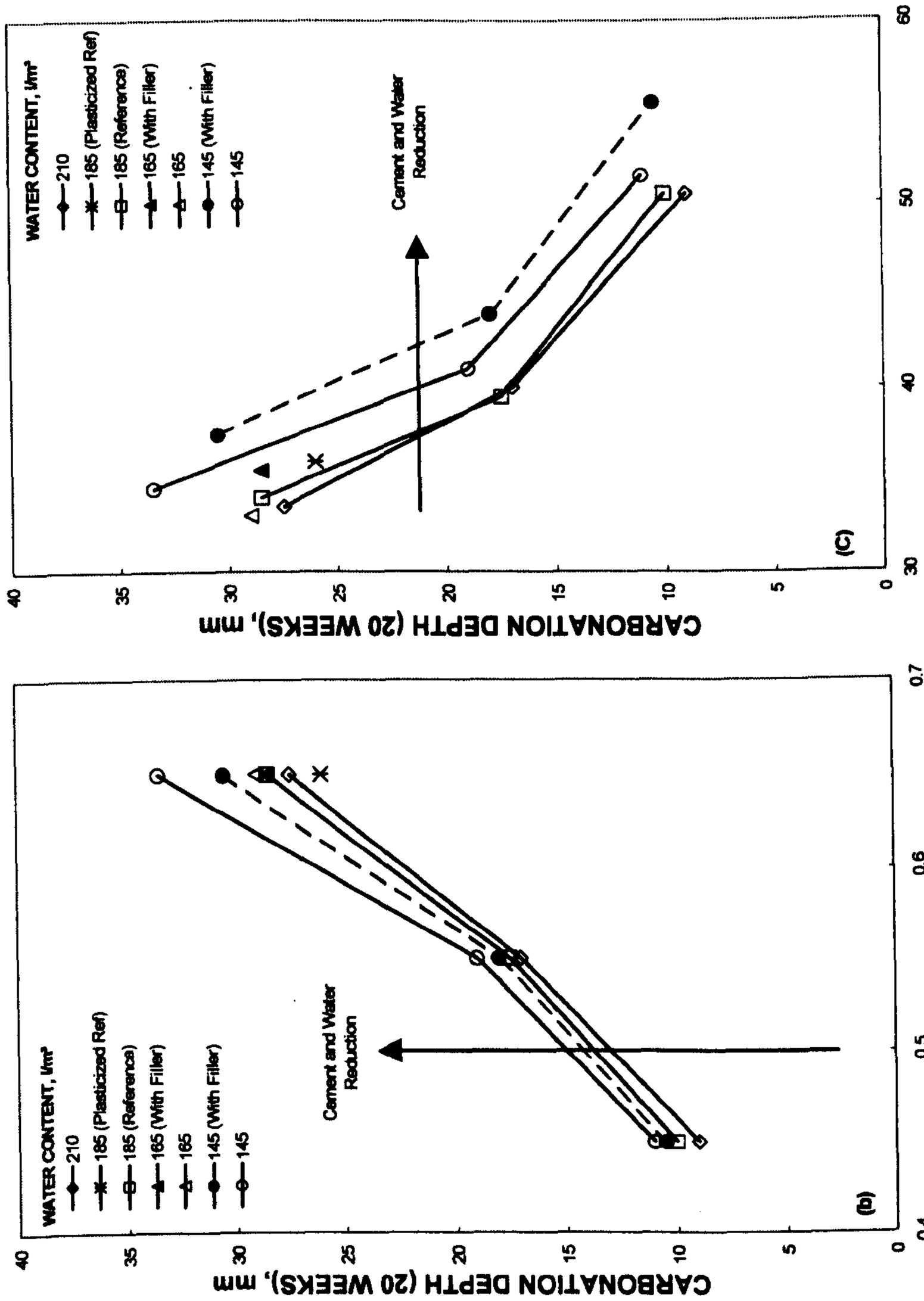


Figure 4.10 Effect of cement content on carbonation resistance of concrete made with dolomitic magnesium limestone coarse aggregate

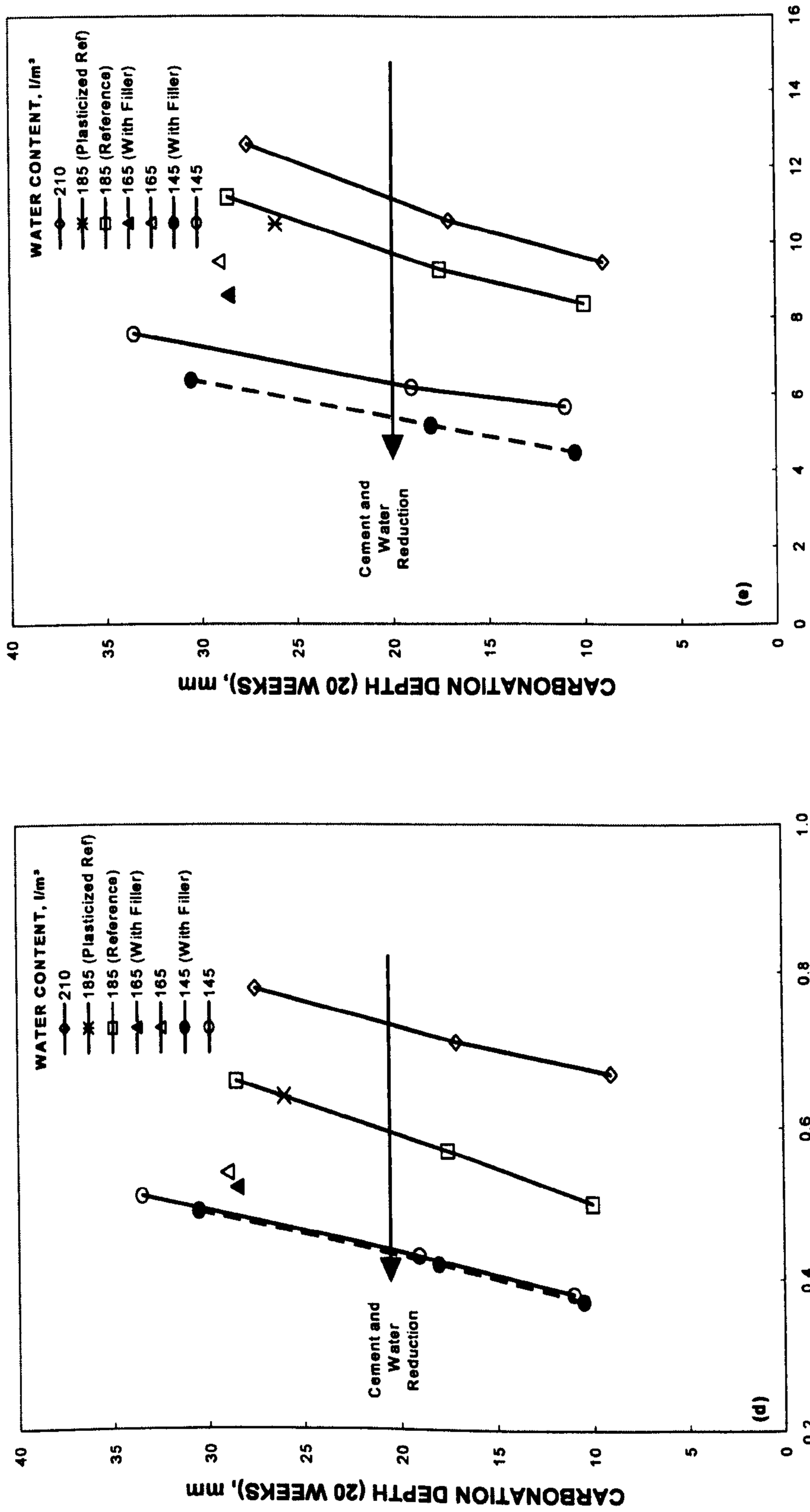


Figure 4.10 Effect of cement content on carbonation resistance of concrete made with dolomitic magnesium limestone coarse aggregate (continued)

In addition, slightly poor performance of cement-and-water-reduced concrete may be due to reduced fines content, as a sufficient quantity of fines is required to achieve a closed structure (*i.e.* concrete microstructure with hydration products having sufficient density and volume to fill the voids) (Harrison, 1997). Indeed, this fact supports the improved performance of cement-and-water-reduced mixes with filler compared to those without filler. Furthermore, the inclusion of limestone filler is likely to provide further benefits with improved quality of the cement paste, possibly due to the mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, reduced bleeding, chemical reactivity and absorption / adsorption characteristics of limestone filler. However, increased aggregate content in cement-and-water-reduced mixes increases the effective ITZ area, which has the highest porosity of the composite. This may also contribute to increase the diffusivity of concrete, although reduced bleeding partly offsets this effect.

The slightly better performance of concrete when superplasticizer is added to increase the workability is possibly due to better deflocculation and dispersion of cement particles and, consequently, better hydration.

Overall, it is worth mentioning that as with other properties discussed earlier, carbonation resistance of concrete is controlled by a number of interconnected factors and it is not easy to isolate them.

4.5.2 Chloride Diffusion

The chloride diffusion coefficients, determined using the PD (potential difference) method, are given in Table 4.14 and plotted in Figures 4.11 (a) to (e) against cement content, w/c ratio, 28-day cube strength, ISA-10 and air permeability, respectively. They agree with most of the trends given in the literature review (Dhir *et al*, 1987a; Dhir *et al*, 1996; McCarthy *et al*, 1996; Buenfeld and Okundi, 1998). At a given w/c ratio;

- Reduction in cement and water contents led to a slight reduction in chloride diffusion coefficient (at all w/c ratios) compared to the Reference Mix (M1) and this effect was greatest when the filler was included to maintain the fines content equal to that of the Reference Mix (M1). Thus, Mix M3*f* resulted in the lowest diffusion coefficient, which was up to 10% lower than the Reference Mix (M1).
- Raising workability from 75 to 180 mm nominal slump through the use of superplasticizer (M4 tested only at w/c ratio 0.45) increased chloride diffusion coefficient slightly (9%) compared to the Reference Mix (M1). When cement and water contents were increased (M5), chloride diffusion coefficient increased (between 1 and 17%) in comparison to the Reference Mix (M1) and this effect was greatest at w/c ratio 0.45.

Table 4.14 Chloride diffusion coefficient of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	CHLORIDE DIFFUSION COEFFICIENT[$] (PD)	
		$cm^2/s \times 10^{-7}$	% of M1
0.65	M5*	31.3	101
	M4*[#]	n/t	n/t
	M1	31.0	100
	M2*f*[#]	n/t	n/t
	M2[#]	n/t	n/t
	M3*f*[#]	28.5	92
	M3[#]	29.0	94
0.55	M5*	23.6	105
	M4*[#]	n/t	n/t
	M1	22.5	100
	M2*f*[#]	n/t	n/t
	M2[#]	n/t	n/t
	M3*f*[#]	20.2	90
	M3[#]	21.0	93
0.45	M5*	20.1	117
	M4*[#]	18.7	109
	M1	17.2	100
	M2*f*[#]	16.4	95
	M2[#]	16.8	98
	M3*f*[#]	16.0	93
	M3[#]	16.6	97

[$] *5 M NaCl exposure at 20°C*
All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] *Superplastizer added to maintain workability*
f Filler included to maintain fines content equal to that of M1
n/t Not tested

As for the carbonation of concrete, the w/c ratio is more important than cement content in controlling chloride diffusion into the concrete.

Given that the porosity of the combined aggregate (mainly consists of coarse aggregate) in concrete is lower than that of the cement paste (in concrete), see Section 4.4.1 (capillary porosity), the chloride diffusion appears to be mainly a paste property. Therefore, reduced volume of cement paste (and increased aggregate volume) with cement and water reduction might be expected to reduce the diffusion coefficient. Indeed, Hobbs (1999) has shown this theoretically. In addition, reduced diffusion coefficients with cement and water reduction are in line with ISA-10 and air permeability results (see Figures 4.11 (d) and (e)), although diffusivity of concrete is not

necessarily directly related to these permeation properties, as mentioned earlier. Moreover, greater tortuosity of flow paths with increased aggregate contents is likely to reduce chloride diffusion into concrete. However, the increased ITZ area (though reduced bleeding partly offsets this effect) and reduced fines content (which controls achieving a closed structure) tend to partly offset the beneficial effects of controlling the chloride diffusion with cement and water reduction. One further factor to be noted is reduced chloride binding capacity with cement reduction. However, as the observed trends indicate a reduction in the chloride diffusion coefficients with reduction in cement and water contents in equal proportion, binding effects seem to be less significant.

The inclusion of limestone filler further reduced the chloride diffusion coefficients, probably due to increased fines content and their contribution to achieving a closed structure. In addition, improved quality of the cement paste, possibly due to mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, reduced bleeding, chemical reactivity and absorption / adsorption characteristics of limestone filler, is likely to contribute to this.

4.5.3 Sulfate Resistance

The sulfate expansion measurements at 98 weeks and expansion plotted against exposure time up to 98 weeks, are given in Table 4.15 and Figure 4.12, respectively. At w/c ratio 0.45;

- For the Reference Mix (M1), no expansion was measured during the first 35 weeks of exposure. After this, expansion increased gradually and expansion strain at 98 weeks was 73×10^{-6}.
- Reduction in cement and water contents without the inclusion of filler (M2 and M3) did not change the initiation time of expansion, but resulted in slightly lower expansions (at a given time after initiation) compared to the Reference Mix (M1). After 98 weeks, reductions for Mixes M2 and M3 were 18 and 25%, respectively, compared to the Reference Mix (M1). When the filler was used to maintain the fines content in the mix (M2*f* and M3*f*), expansion initiation was delayed by a further 29 weeks compared to the Reference Mix (M1) and, once initiated, expansion tended to occur at a lower rate. After 98 weeks of exposure, expansions of Mixes M2*f* and M3*f* were reduced by 64 and 70%, respectively, in comparison to the Reference Mix (M1).
- When workability was raised from 75 to 180 mm nominal slump through the use of superplasticizer (M4), or when cement and water contents were increased (M5), expansion initiation and rate of expansion were almost unchanged compared to the Reference Mix (M1). Thus, Mixes M4 and M5 increased expansion strain at 98 weeks by 8 and 4%, respectively, compared to the Reference Mix (M1).

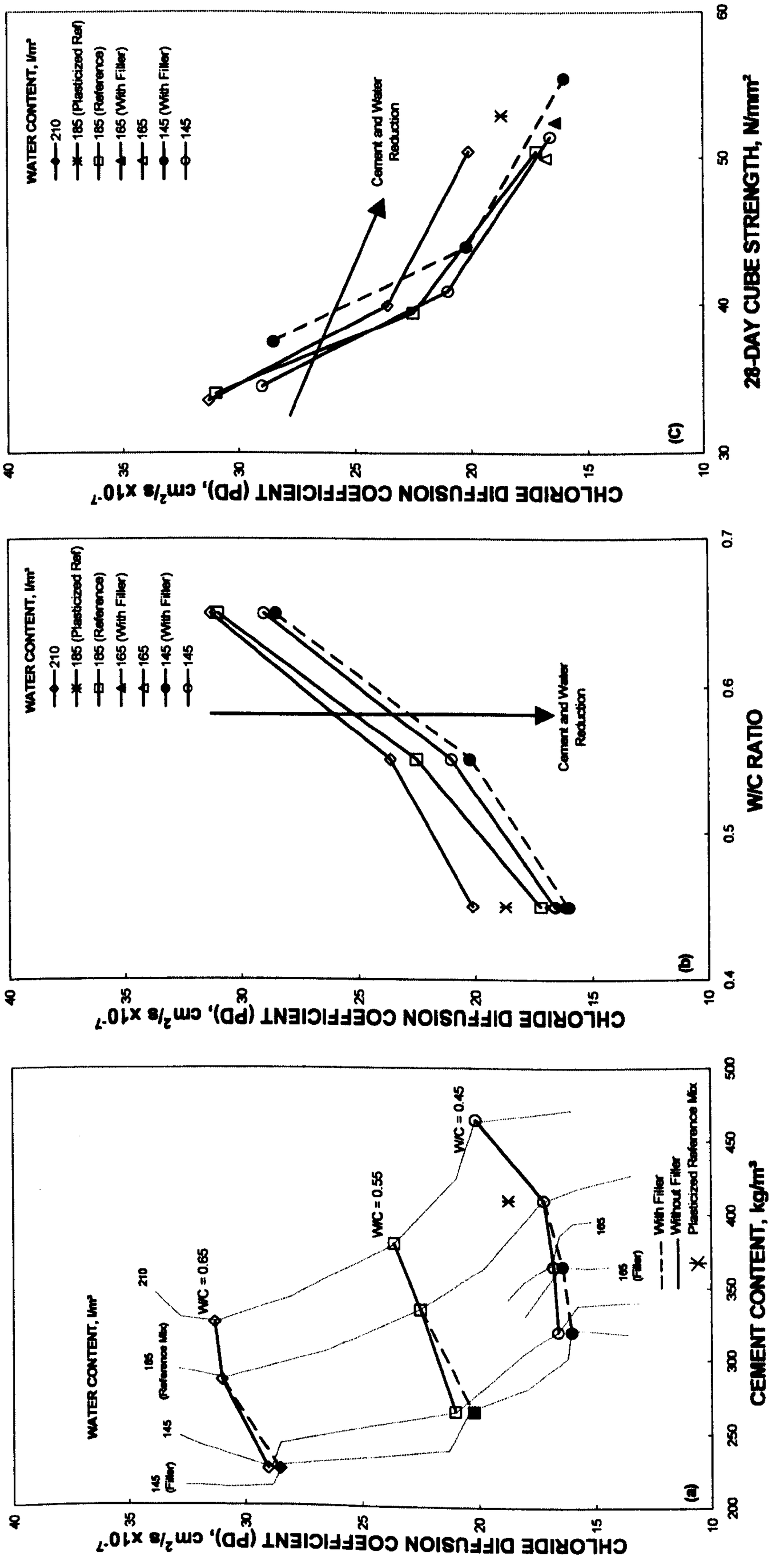


Figure 4.11 Effect of cement content on chloride diffusion coefficient of concrete made with dolomitic magnesium limestone coarse aggregate

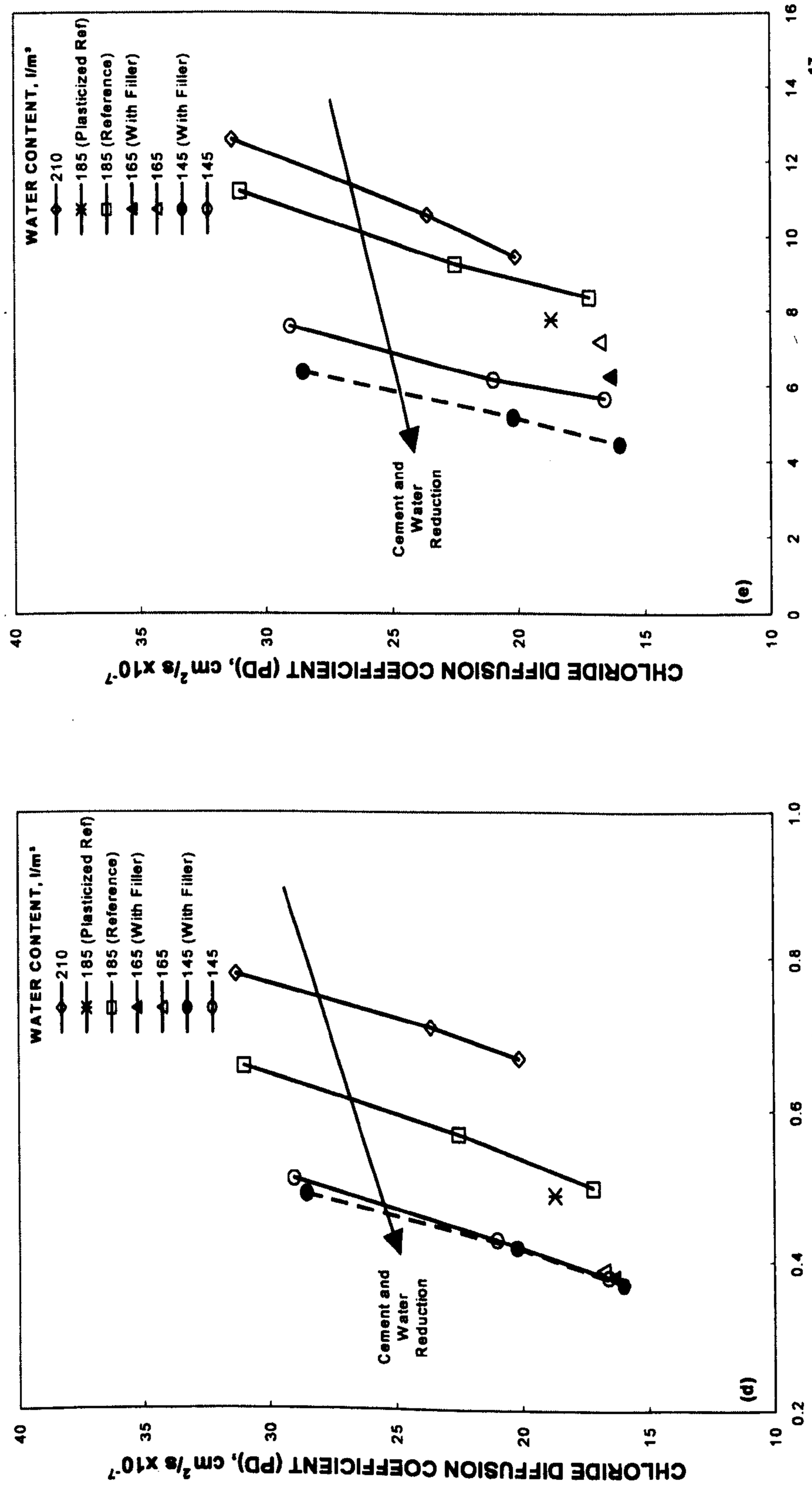


Figure 4.11 Effect of cement content on chloride diffusion coefficient of concrete made with dolomitic magnesium limestone coarse aggregate (continued)

Table 4.15 Sulfate resistance of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	SULFATE EXPANSION[$] (98 WEEKS)	
		Strain x 10^{-6}	% of M1
0.45	M5*	76	104
	M4*[#]	79	108
	M1	73	100
	M2*f*[#]	26	36
	M2[#]	60	82
	M3*f*[#]	22	30
	M3[#]	55	75

[$] *5% Na_2SO_4 exposure at 20°C*
All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] *Superplastizer added to maintain workability*
f Filler included to maintain fines content equal to that of M1

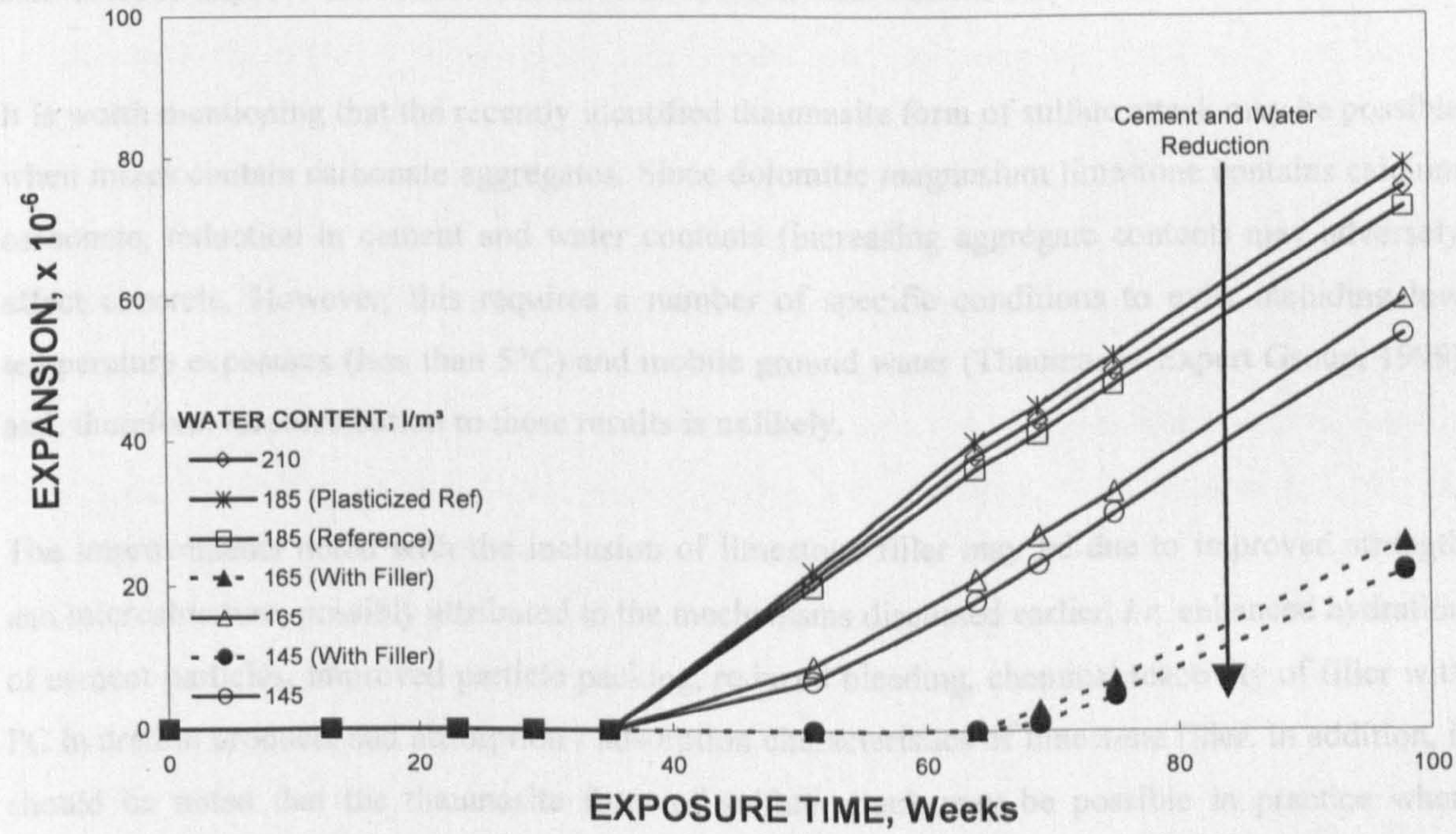


Figure 4.12 Sulfate expansion of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.45

Sulfate expansion with variation in cement and water contents in equal proportion is in line with the compressive strength results discussed in Section 4.3.1. Before discussing the results, it should be noted that expansion may be partly attributed to swelling of concrete. Indeed, L'Hermite (1960) observed typical expansions of 100 to 150 x 10^{-6} due to swelling when concrete specimens were immersed in water for 1 year. The observed results in this study, after 98 weeks of exposure to a

5% sodium sulfate ($Na_2SO_4 .10H_2O$) solution at 20°C, varied between 22 and 79 x 10^{-6} and, therefore, it appears that variation in cement and water contents in equal proportion may have little or no influence on sulfate expansion and that the results may be attributed to possible test variabilities. Indeed, after 98 weeks, specimens (for all mixes) did not show any visual sign of deterioration. In addition, the results suggest that 5% sodium sulfate solution may not be strong enough to cause any expansion for the test period used. However, it is worth exploring possible mechanisms controlling sulfate expansion with variation in cement and water contents.

Given that sulfate ions attack the cement paste (rather than the aggregates), reduction in cement and water contents in equal proportion (increasing aggregate content) would be expected to be beneficial and this was the observed behaviour. In addition, reduced bleeding and number of bleed channels, which tend to eliminate weak zones and w/c ratio gradients, are likely to improve the sulfate resistance of concrete with cement and water reduction. However, this effect may be partly offset by the increased effective ITZ area (see the discussion given in Section 4.3.1). Moreover, possible improvements to the concrete microstructure (as noted in the permeation properties) can contribute to improve the sulfate resistance of concrete with cement and water reduction.

It is worth mentioning that the recently identified thaumasite form of sulfate attack may be possible when mixes contain carbonate aggregates. Since dolomitic magnesium limestone contains calcium carbonate, reduction in cement and water contents (increasing aggregate content) may adversely affect concrete. However, this requires a number of specific conditions to exist including low temperature exposures (less than 5°C) and mobile ground water (Thaumasite Expert Group, 1999) and, therefore, its contribution to these results is unlikely.

The improvements noted with the inclusion of limestone filler may be due to improved strength and microstructure, possibly attributed to the mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, reduced bleeding, chemical reactivity of filler with PC hydration products and absorption / adsorption characteristics of limestone filler. In addition, it should be noted that the thaumasite form of sulfate attack may be possible in practice when limestone filler is used (though these results were not affected), as concrete is likely to be subjected to varying conditions.

The minor differences in performance compared to the Reference Mix (M1) when workability was raised from 75 to 180 mm nominal slump through the use of superplasticizer, or when cement and water contents were increased in equal proportion, may be due to possible test variabilities. Indeed, Ali (1996) suggests that the use of superplasticizer is unlikely to affect the sulfate resistance of concrete.

4.5.4 Freeze / Thaw Resistance

The cumulative quantities of scaled material collected after 28 and 56 test cycles for specimens exposed up to 56 freeze / thaw cycles with a 3.0% sodium chloride (NaCl) test solution are given in Tables 4.16 (a) and (b), respectively. The cumulative scaling is plotted in Figure 4.13 against the number of test cycles. The results obtained with variation in cement and water contents in equal proportion are generally in line with previous studies given in the literature review (Dhir *et al*, 1987a; Basheer *et al*, 1994). At w/c ratio 0.45;

- The Reference Mix (M1) resulted in an accumulated scaling of 0.77 kg/m² after 56 test cycles.
- Reduction in cement and water contents without the inclusion of filler (M2 and M3) reduced cumulative scaling at all test ages compared to the Reference Mix (M1). This reduction after 56 test cycles was 53 and 57% for Mixes M2 and M3, respectively. When the filler was used to maintain the fines content in the mix (M2*f* and M3*f*), cumulative scaling at a given exposure time was higher than that of the Reference Mix (M1). The results (after 56 cycles) for Mixes M2*f* and M3*f* were 57 and 90% higher, respectively, compared to the Reference Mix (M1).
- Raising workability from 75 to 180 mm nominal slump with the use of superplasticizer (M4) improved freeze / thaw resistance and cumulative scaling after 56 cycles was 51% of that of the Reference Mix (M1). When cement and water contents were increased with workability increase from 75 to 180 mm nominal slump (M5), slight reductions in freeze / thaw scaling (typically about 20%) were obtained in comparison to the Reference Mix (M1).

The improved freeze / thaw resistance with reduction in cement and water contents in equal proportion compared to the Reference Mix (M1), may be due to reduced capillary porosity and improved concrete microstructure (see Section 4.4) and, thus, less accommodated water under wet conditions. In addition, reduced free water contents and, therefore, lower expansion forces on freezing of cement-and-water-reduced mixes may contribute to this. However, it should be noted that increased effective ITZ area with cement reduction (increasing aggregate content), marked by a greater porosity, which is possibly accompanied by increased content of freezable water, may partly offset the beneficial effects.

It is worth mentioning that if excess water can readily escape into adjacent air-filled voids, freeze / thaw damage can be minimised. However, this applies only if the volume of capillary pores is minimised in the first place, otherwise the amount of freezable water would exceed that which can be accommodated by the entrained air (Neville, 1995). Therefore, increased air contents (when expressed as percentages by volume of cement paste) with cement and water reduction may also contribute to improve the freeze / thaw resistance.

Table 4.16 Freeze / thaw resistance of concrete made with dolomitic magnesium limestone coarse aggregate (in the presence of 3% NaCl solution)

(a) After 28 test cycles[$]

W/C RATIO	MIX	CUMULATIVE SCALING	
		kg/m^2	% of M1
0.45	M5*	0.42	84
	M4*#	0.28	56
	M1	0.50	100
	M2*f*#	0.62	124
	M2#	0.25	50
	M3*f*#	0.72	144
	M3#	0.22	44

(b) After 56 test cycles[$]

W/C RATIO	MIX	CUMULATIVE SCALING	
		kg/m^2	% of M1
0.45	M5*	0.60	78
	M4*#	0.39	51
	M1	0.77	100
	M2*f*#	1.21	157
	M2#	0.36	47
	M3*f*#	1.46	190
	M3#	0.33	43

[$] 1 test cycle: +20 to -20 to +20 ℃ over 24 hours
All mixes contain PC, 42.5 N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

The inclusion of limestone filler may have been expected to be beneficial to freeze / thaw resistance, given its effect on most other concrete properties. However, improved quality of the cement paste due to improved particle packing and other beneficial effects, probably tends to restrict water movement and expansion and, consequently, to increase expansive stresses.

The better performance compared to the Reference Mix (M1) when raising workability from 75 to 180 mm nominal slump using superplasticizer may be due to better deflocculation and dispersion of cement particles and, consequently, improved pore distribution, as this did not change permeation properties and air content significantly compared to the Reference Mix (M1). The slightly improved freeze / thaw resistance when cement and water contents were increased in equal

proportion may be associated with test variabilities. However, this difference in performance between Mixes M5 and M1 appears to be minor.

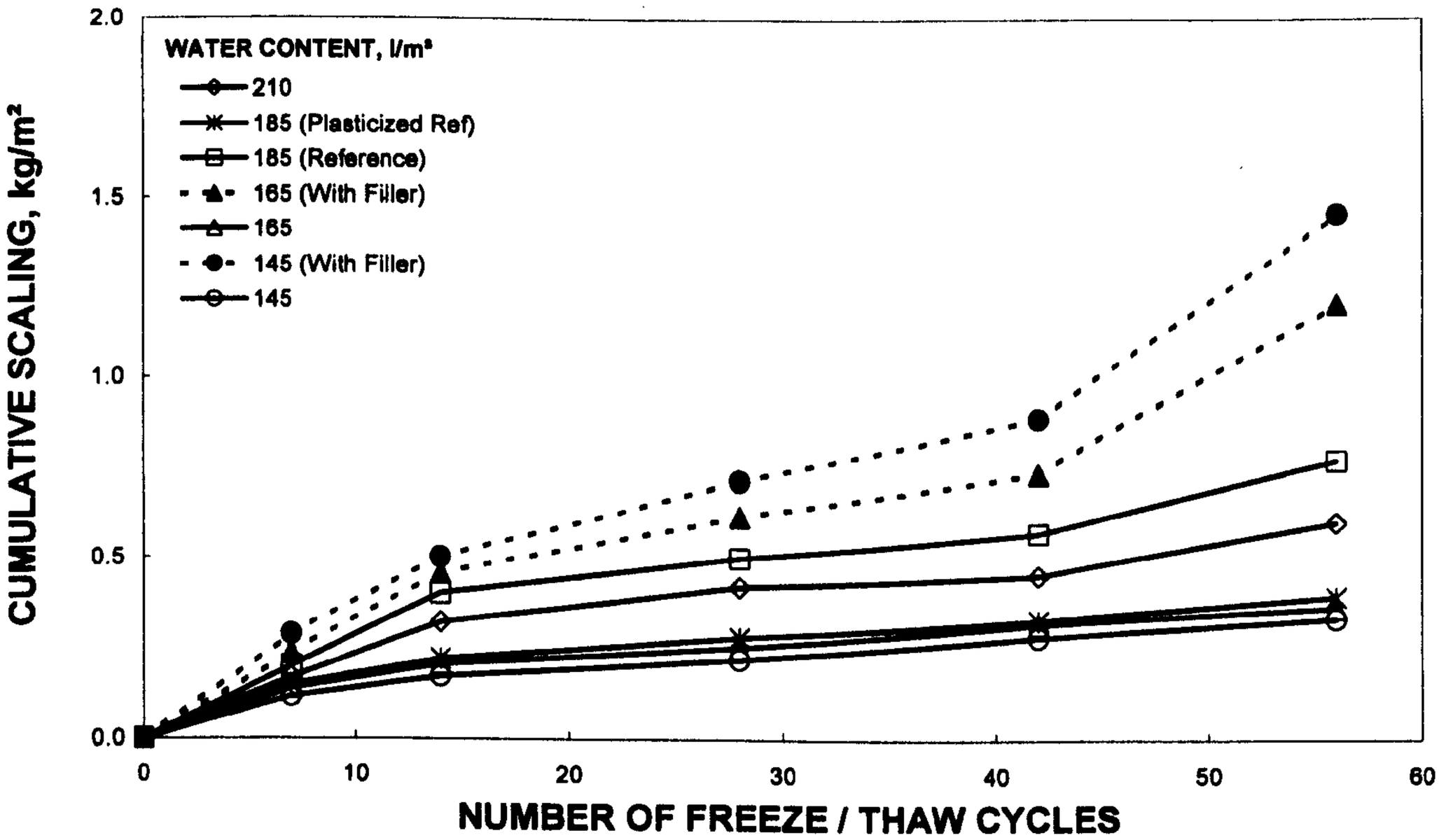


Figure 4.13 Cumulative freeze / thaw scaling of concrete made with dolomitic magnesium limestone coarse aggregate, w/c ratio = 0.45

4.5.5 Abrasion Resistance

The abrasion depth measurements are given in Table 4.17. The results agree with previous work given in the literature review (Dhir *et al*, 1991). The main points to note are, at w/c ratio 0.50;

- The abrasion depth measured for the Reference Mix (M1) was 0.89 mm.
- Reduction in cement and water contents led to improved abrasion resistance compared to the Reference Mix (M1) and this effect was greatest when the filler was included to maintain the fines content equal to that of the Reference Mix (M1). Thus, Mix M3*f* resulted in the lowest abrasion depth, which was 31% lower than that of the Reference Mix (M1).
- The use of superplasticizer to raise workability from 75 to 180 mm nominal slump (M4) led to a slight reduction in abrasion depth by 6% compared to the Reference Mix (M1), whilst an increase of 7% was obtained when cement and water contents were increased (M5).

Table 4.17 Abrasion resistance of concrete made with dolomitic magnesium limestone coarse aggregate

W/C RATIO	MIX	ABRASION DEPTH	
		mm	% of M1
0.50	M5*	0.95	107
	M4*#	0.84	94
	M1	0.89	100
	M2*f*#	0.62	70
	M2#	0.67	75
	M3*f*#	0.61	69
	M3#	0.64	72

All mixes contain PC, 42.5N and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Abrasion resistance of concrete mainly depends on the strength and hardness of the surface zone (Neville, 1995). Therefore, it appears that mechanisms associated with increasing compressive strength with reduction in cement and water contents in equal proportion are likely to contribute to improve abrasion resistance. Indeed, improved quality (thus, hardness) of cement paste (as reflected by permeation properties), increased aggregate volume (stronger component) and reduced cement paste (weaker component), and improved surface quality due to reduced bleeding, all tend to increase the abrasion resistance of concrete. Indeed, observed abrasion depths with cement and water reduction are closely related to the compressive strength.

The inclusion of limestone filler further improved abrasion resistance with improved quality (hence hardness) of the cement paste, possibly due to mechanisms discussed earlier, *i.e.* enhanced hydration of cement particles, improved particle packing, chemical reactivity and absorption / adsorption characteristics of limestone filler.

The slightly improved abrasion resistance when workability was raised from 75 to 180 mm nominal slump through addition of superplasticizer may be due to better deflocculation and dispersion of cement particles and, consequently, improved compressive strength.

4.6 CONCLUSIONS

The following conclusions can be drawn from the results in this chapter. Unless otherwise stated, they are based on concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate. Note that a discussion of the practical implications of these conclusions is given in Chapter 8.

4.6.1 Fresh Properties

- Reference Mixes exhibited good cohesion. A 20 l/m^3 water (and corresponding cement) reduction at fixed w/c ratio with-or-without limestone filler made no changes to the cohesion of concrete compared to the Reference Mix, but a 40 l/m^3 water reduction resulted in a loss of cohesion. However, the inclusion of filler (with a 40 l/m^3 water reduction) to maintain the fines content equal to that of the Reference Mix, resulted in a slight regain of cohesion. At fixed w/c ratio, raising workability using superplasticizer or increasing cement and water contents with increased workability, led to a higher cohesion in comparison to that of the Reference Mix.

- The trends seen with cohesion generally reflected in the finishability characteristics of concrete. As a result, cement and water reduction in equal proportion required more effort to achieve finishability. As before, the inclusion of limestone filler was beneficial. At fixed w/c ratio, raising workability through the use of superplasticizer or increasing cement and water contents with increased workability, generally led to improved finishability compared to the Reference Mix.

- Reduction in cement and water contents in equal proportion, either with-or-without limestone filler to maintain the fines content equal to that of the Reference Mix, had no significant influence on air content of concrete compared to the Reference Mix. At fixed w/c ratio, raising workability through the use of superplasticizer or increasing cement and water contents with increased workability, led to no significant change in air content compared to the Reference Mix.

- A 40 l/m^3 water (and corresponding cement) reduction at fixed w/c ratio delayed bleeding initiation and reduced cumulative bleeding significantly compared to the Reference Mix. This beneficial effect was more pronounced when the filler was included to maintain the fines content and no bleeding was recorded after 2 hours. When cement and water contents were increased in equal proportion with increased workability, bleeding tended to increase compared to the Reference Mix.

4.6.2 Engineering Properties

- Compressive strength generally increased with reduction in cement and water contents in equal proportion. This effect was more pronounced when the filler was used to maintain the fines content equal to that of the Reference Mix. At fixed w/c ratio, when cement and water contents were increased, with increased workability, strength was almost unaffected in comparison to the Reference Mix, whilst generally minor strength gains were noted with the

use of superplasticizer to give high workability. The w/c ratio remained the main influencing factor for compressive strength, not the cement content.

- In general, reduction in cement and water contents in equal proportion had no adverse effect on flexural strength. The inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix, with cement and water reduction, resulted in slightly higher flexural strengths compared to the Reference Mix. This effect was most notable at lower w/c ratios. At fixed w/c ratio, raising workability through the use of superplasticizer had no clear influence on the flexural strength compared to the Reference Mix. However, increasing cement and water contents in equal proportion with increased workability resulted in a slight reduction in flexural strength. Moreover, reducing cement and water contents in equal proportion slightly reduced the flexural / compressive strength ratio, suggesting there was a tendency for increased brittleness.

- The modulus of elasticity generally increased with reduction in cement and water contents in equal proportion. The addition of limestone filler to maintain the fines content equal to that of the Reference Mix, with cement reduction, further increased the modulus of elasticity. At fixed w/c ratio, raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, resulted in a slight increase and decrease in modulus of elasticity, respectively, compared to the Reference Mix.

- Reduction in cement and water contents in equal proportion gave slightly higher maximum stresses and lower corresponding strains, particularly when the filler was included to maintain the fines content equal to that of the Reference Mix, reflecting the slightly higher stiffness obtained by concrete with higher compressive strengths. Increasing cement and water contents in equal proportion with increased workability had only a minor effect on the stress / strain characteristics of concrete in comparison to the Reference Mix.

- Reduction in cement and water contents in equal proportion reduced drying shrinkage in comparison to the Reference Mix. This effect tended to be slightly greater for mixes where the filler was used to maintain the fines content equal to that of the Reference Mix. At fixed w/c ratio, raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, led to a minor increase and considerable increase in shrinkage, respectively, compared to the Reference Mix.

4.6.3 Permeation Properties

- Capillary porosity decreased with reducing cement and water contents in equal proportion. This effect tended to be greater for mixes where the filler was used to maintain the fines content equal to that of the Reference Mix. When cement and water contents were increased in equal proportion with increased workability, porosity increased slightly compared to the Reference Mix and this was greatest at w/c ratio 0.55 (higher w/c ratio). The above observations were not influenced by aggregate or cement type. However, for a given mix, capillary porosity increased with increasing water absorption of aggregates. The use of PC / PFA and PC / GGBS reduced the capillary porosity compared to equivalent mixes made with PC, 42.5 N and this effect was greatest at w/c ratio 0.55 (higher w/c ratio). Moreover, for a given mix, the porosity of concrete made with PC / GGBS was slightly lower than that of PC / PFA.

- Capillary porosity results reflected in the water absorption results of concrete. As a result, cement and water reduction in equal proportion reduced water absorption. As before, this effect tended to be greater for mixes where the filler was used to maintain the fines content equal to that of the Reference Mix. At fixed w/c ratio, when cement (and hence water) content was increased, with increased workability, water absorption slightly increased compared to the Reference Mix. The trends noted with variation in cement and water contents were essentially similar for concrete made with different aggregate and cement types. However, for a given mix, the water absorption of concrete increased with increasing water absorption of aggregates. Furthermore, the effect of cement and water reduction was more pronounced for concrete made with PC / limestone compared to that made with PC and other aggregate types. In addition, concrete made with PC / PFA and PC / GGBS led to reduced water absorption of concrete (compared to equivalent mixes made with PC, 42.5 N), whilst the performance of PC / GGBS was slightly better than that of PC / PFA. This effect was most notable at w/c ratio 0.45 (lower w/c ratio). Moreover, the influence of cement and water reduction was more pronounced for concrete made with PC compared to that made with PC / PFA or PC / GGBS.

- Initial surface absorption results were in line with the capillary porosity and water absorption results, *i.e.* ISA-10 progressively reduced with cement and water reduction in equal proportion and was least for mixes having the filler to maintain the fines content equal to that of the Reference Mix. When superplasticizer was used to raise workability, ISA-10 reduced slightly compared to the Reference Mix. However, when cement and water contents were increased in equal proportion with increased workability, ISA-10 increased in comparison to the Reference Mix and this effect was most notable at lower w/c ratios. The above observations were not influenced by aggregate or cement type. However, as for other permeation properties, for a given mix, ISA-10 of concrete increased with increasing water absorption of aggregates.

Furthermore, when cement and water contents were increased, PC / limestone concrete showed a more pronounced increase in ISA-10 compared to concrete made with PC and other aggregate types. In addition, the use of PC / PFA and PC / GGBS reduced the ISA-10 compared to equivalent mixes made with PC, 42.5 N and the performance of concrete made with PC / GGBS was slightly better than that of PC / PFA.

- The changes occurring in air permeability with variation in cement and water contents in equal proportion were essentially similar to those noted for capillary porosity, water absorption and ISA-10, *i.e.* air permeability gradually reduced with cement and water reduction and was least for mixes with the filler to maintain the fines content equal to that of the Reference Mix. Raising workability using superplasticizer had only a minor influence on air permeability in comparison to the Reference Mix with a slight reduction. As before, when cement and water contents were increased in equal proportion with increased workability, air permeability increased in comparison to the Reference Mix.

4.6.4 Durability Properties

- When cement and water contents were reduced in equal proportion, carbonation depth tended to be slightly higher than that of the Reference Mix. This effect was most notable when the fines content was allowed to deplete (at higher w/c ratios, *e.g.* 0.65), however, this was partly offset with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix. When workability was raised through the use of superplasticizer (tested only at w/c ratio 0.65), or when cement and water contents were increased in equal proportion with increased workability, carbonation depth reduced slightly compared to the Reference Mix. Moreover, the cement content had a little influence on the carbonation resistance of concrete compared to the w/c ratio, which was the main influencing factor.

- Reduction in cement and water contents in equal proportion led to a slight reduction in the chloride diffusion coefficient compared to the Reference Mix and this effect was greatest when the filler was included to maintain the fines content equal to that of the Reference Mix. Raising workability through the use of superplasticizer (tested only at w/c ratio 0.45) increased chloride diffusion coefficient slightly compared to the Reference Mix. Furthermore, when cement and water contents were increased in equal proportion with increased workability, chloride diffusion coefficient increased in comparison to the Reference Mix and this effect was greatest at lower w/c ratios. Moreover, the w/c ratio remained the main influencing factor in controlling the chloride diffusion coefficient of concrete, not the cement content.

- Reduction in cement and water contents in equal proportion led to improved sulfate resistance compared to the Reference Mix and this effect was more significant when the filler was included to maintain the fines content equal to that of the Reference Mix. When workability was raised through the use of superplasticizer, or when cement and water contents were increased in equal proportion with increased workability, expansion initiation and rate of expansion were almost unchanged compared to the Reference Mix.

- Reduction in cement and water contents in equal proportion without the inclusion of filler, improved freeze / thaw resistance of concrete compared to the Reference Mix. However, when the filler was used to maintain the fines content equal to that of the Reference Mix, freeze / thaw resistance was reduced significantly compared to the Reference Mix. Raising workability through the use of superplasticizer increased freeze / thaw resistance in comparison to the Reference Mix. When cement and water contents were increased in equal proportion with workability increase, a minor change in freeze / thaw scaling was observed in comparison to the Reference Mix.

- Reduction in cement and water contents in equal proportion led to improved abrasion resistance compared to the Reference Mix and this effect was greatest when the filler was included to maintain the fines content equal to that of the Reference Mix. The use of superplasticizer to raise workability led to a slight improvement in abrasion resistance compared to the Reference Mix, whilst a slightly reduced resistance was obtained when cement and water contents were increased in equal proportion with workability increase.

CHAPTER 5

ROLE OF CEMENT CONTENT ON RESISTANCE OF CONCRETE TO CARBONATION-INDUCED REINFORCEMENT CORROSION

5.1 INTRODUCTION

The significance of carbonation-induced corrosion as a durability problem in reinforced concrete structures was discussed in the literature review (see Sections 2.3.1 and 2.3.2). However, it is clear that much of the available literature covers only the first phase of the overall deterioration process, *i.e.* role of cement content at fixed w/c ratio on the carbonation of concrete or time to corrosion initiation (see Section 2.4.4). No work appears to have been carried out on the corrosion propagation process related to the influence of cement content at fixed w/c ratio. In addition, it is worth mentioning that a review of published literature indicates that the abundance of carbonation measurements is not matched with measurements of corrosion in carbonated concrete (Parrott, 1987). Therefore, the influence of minimum cement content requirement on the resistance of concrete to carbonation-induced reinforcement corrosion needs to be examined and, indeed, the importance of this has been suggested by several researchers (Harrison, 1997; Hobbs, 1998; Concrete Society, 1999).

Given this background, this study was focused on the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the resistance of concrete to carbonation-induced reinforcement corrosion using small-scale, 100 mm cube specimens. The programme of study, which includes concrete mix details, curing conditions and properties tested, was discussed in Chapter 3 (see Stage 2, carbonation-induced corrosion). As mentioned previously, a range of cement and coarse aggregate combinations was used. PC, 42.5 N, the main cement type, was used with (i) natural gravel, (ii) granite and (iii) dolomitic magnesium limestone. The main coarse aggregate type, dolomitic magnesium limestone, was combined with (i) 100% PC, (ii) 70% PC / 30% PFA and (iii) 50% PC / 50% GGBS. Following the guidelines given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), a w/c ratio of 0.55 was used for all concrete types. The cement content was varied below and above the minimum cement contents given in these standards. For all specimens, the uppermost surface at casting was selected as the test face because the direction of casting is likely to represent the weakest and, therefore, the critical face in terms of damage to the embedded steel. As described earlier in Sections 3.6.4 and 3.6.5, reinforced concrete specimens and sacrificial plain concrete specimens (used to determine the carbonation rate) were air-cured (at 20°C and 55% RH) for 28 days to accelerate subsequent carbonation at 4% carbon dioxide (CO_2) environment (at 20°C and 55% RH). When carbonated to

a depth of 35 mm (*i.e.* cover plus bar diameter), reinforced concrete specimens were transferred to a high humidity environment (20°C, 95% RH) to induce reinforcement corrosion (up to 24 weeks), as the corrosion rate is highest at about 95% RH (Parrott, 1987). Monitoring of corrosion initiation and propagation was made using corrosion potential and polarisation resistance measurements immediately prior to, and at different times during the post-carbonation exposure. After 24 weeks, the cubes were split and the reinforcement was recovered for visual examination. The methods used to assess corrosion potential, polarisation resistance and visual assessment were discussed in Sections 3.6.6.

It should be noted that the scope of this stage is determining the influence of cement content on resistance of concrete to carbonation-induced reinforcement corrosion, not the influence of coarse aggregate and cement type. However, as a range of cement and coarse aggregate types was used, for the convenience of the discussion, the results obtained with concrete made with different coarse aggregate and cement types are presented separately.

5.2. RESULTS AND DISCUSSION

The Reference Mix (M1), the cement-and-water-increased mix with 180 mm nominal slump (M5) and the cement-and-water-reduced (a 40 l/m^3 water reduction) mix with limestone filler (M3*f*) to maintain the fines content equal to that of the Reference Mix (M1), were used for all aggregate-cement combinations. For the main aggregate-cement combination (dolomitic magnesium limestone and PC), two additional mixes, M2 (a 20 l/m^3 water reduction) and M2*f* (a 20 l/m^3 water reduction with the fines content maintained) were considered to cover an intermediate cement content between Mixes M1 and M3*f*, and to examine the effect of cement reduction with-and-without the maintained fines content.

5.2.1 Carbonation Resistance

Before focusing on the carbonation resistance of the concrete mixes mentioned above, it is worth noting that the compressive strength may be used as an alternative basis for the comparison of rate of carbonation (Parrott, 1987). Therefore, 28-day compressive strengths of water-cured (20°C), 100 mm cube specimens were also tested, together with the main work for all the concrete types. The results are given in Tables 5.1 (a) and (b) for concrete made with different coarse aggregate and cement types, respectively. The minor differences between the 28-day compressive strengths of PC / limestone concrete given here and in Section 4.3.1, may be due to variability between batches of concrete.

Figures 5.1 (a) and (b) show the carbonation depth measurements plotted against the square root of the exposure period (4% CO_2 environment at 20°C and 55% RH) for concrete made with different

coarse aggregate types (up to 24 weeks) and cement types (up to 20 weeks), respectively. As expected, carbonation depth was approximately proportional to the square root of exposure time. The final carbonation depths for concrete made with different coarse aggregate types (measured after 24 weeks) and cement types (measured after 20 weeks) are given in Tables 5.2 (a) and (b), respectively. It should be noted that previous studies given in the literature review have been mostly carried out using good quality aggregates and after good curing conditions. The carbonation results given here generally agree with them, except slightly higher carbonation depths observed for PC / limestone concrete with reduction in cement and water contents in equal proportion.

Table 5.1 Comparison of 28-day compressive strength of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	28-DAY CUBE STRENGTH					
		N/mm²			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
0.55	M5*	38.5	42.5	37.5	96	94	95
	M1	40.0	45.0	39.5	100	100	100
	M2*f*#	n/t	n/t	40.0	n/t	n/t	101
	M2#	n/t	n/t	37.0	n/t	n/t	94
	M3*f*#	50.0	55.0	43.0	125	122	109

(b) Made with different cement types

W/C RATIO	MIX	28-DAY CUBE STRENGTH					
		N/mm²			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
0.55	M5*	37.5	30.0	34.5	95	95	97
	M1	39.5	31.5	35.5	100	100	100
	M2*f*#	40.0	n/t	n/t	101	n/t	n/t
	M2#	37.0	n/t	n/t	94	n/t	n/t
	M3*f*#	43.0	34.0	38.5	109	108	108

All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

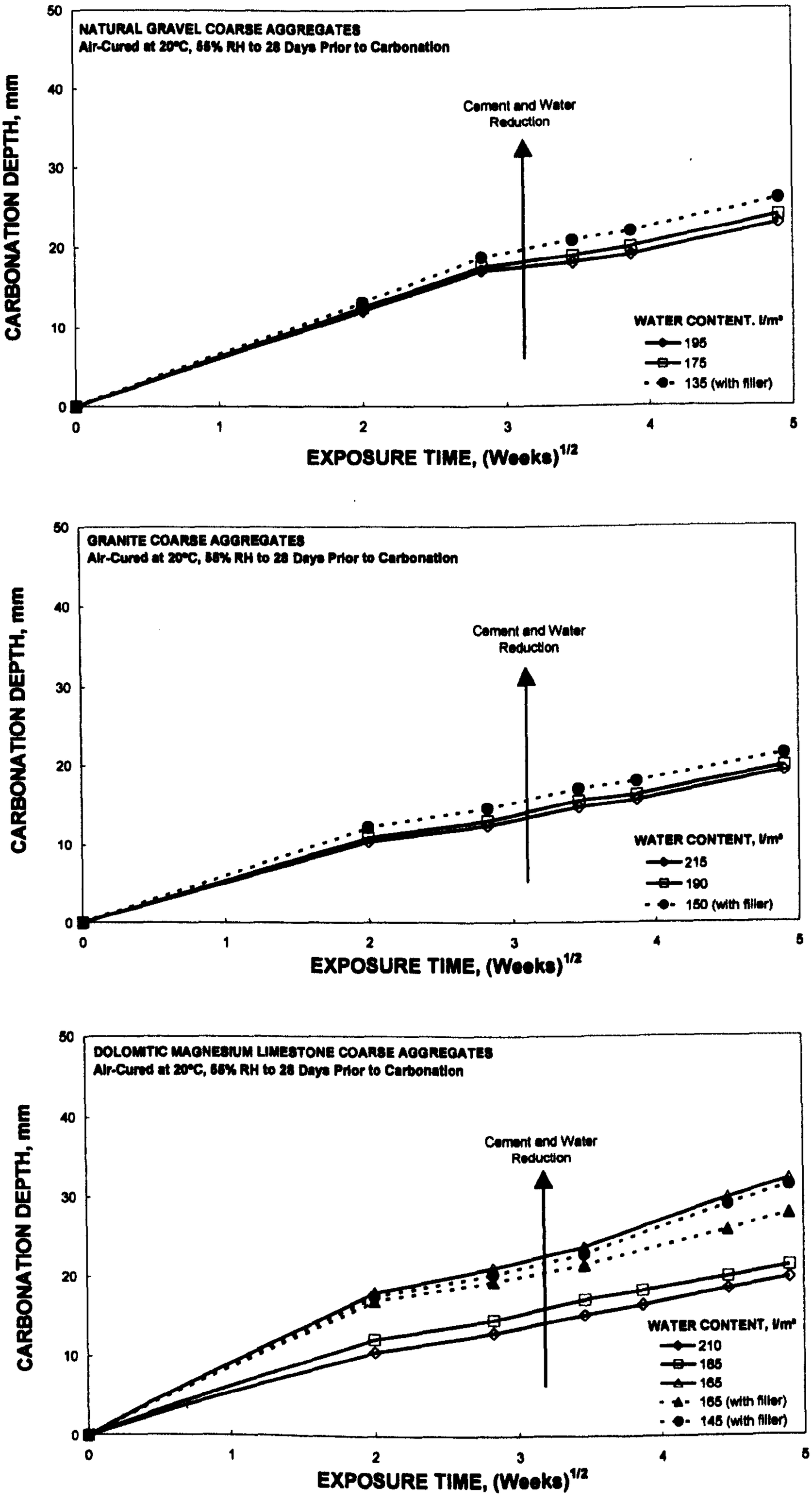
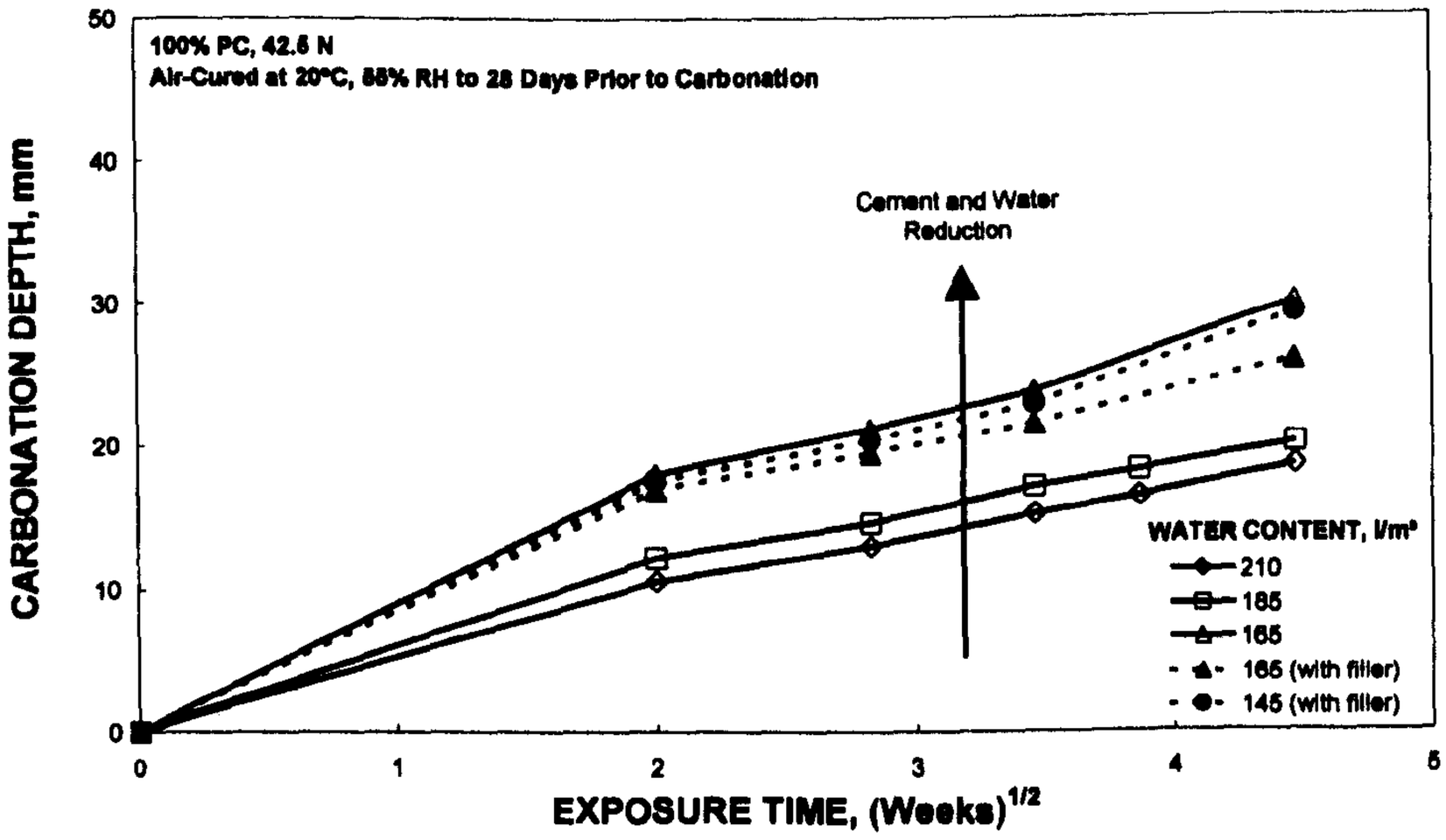
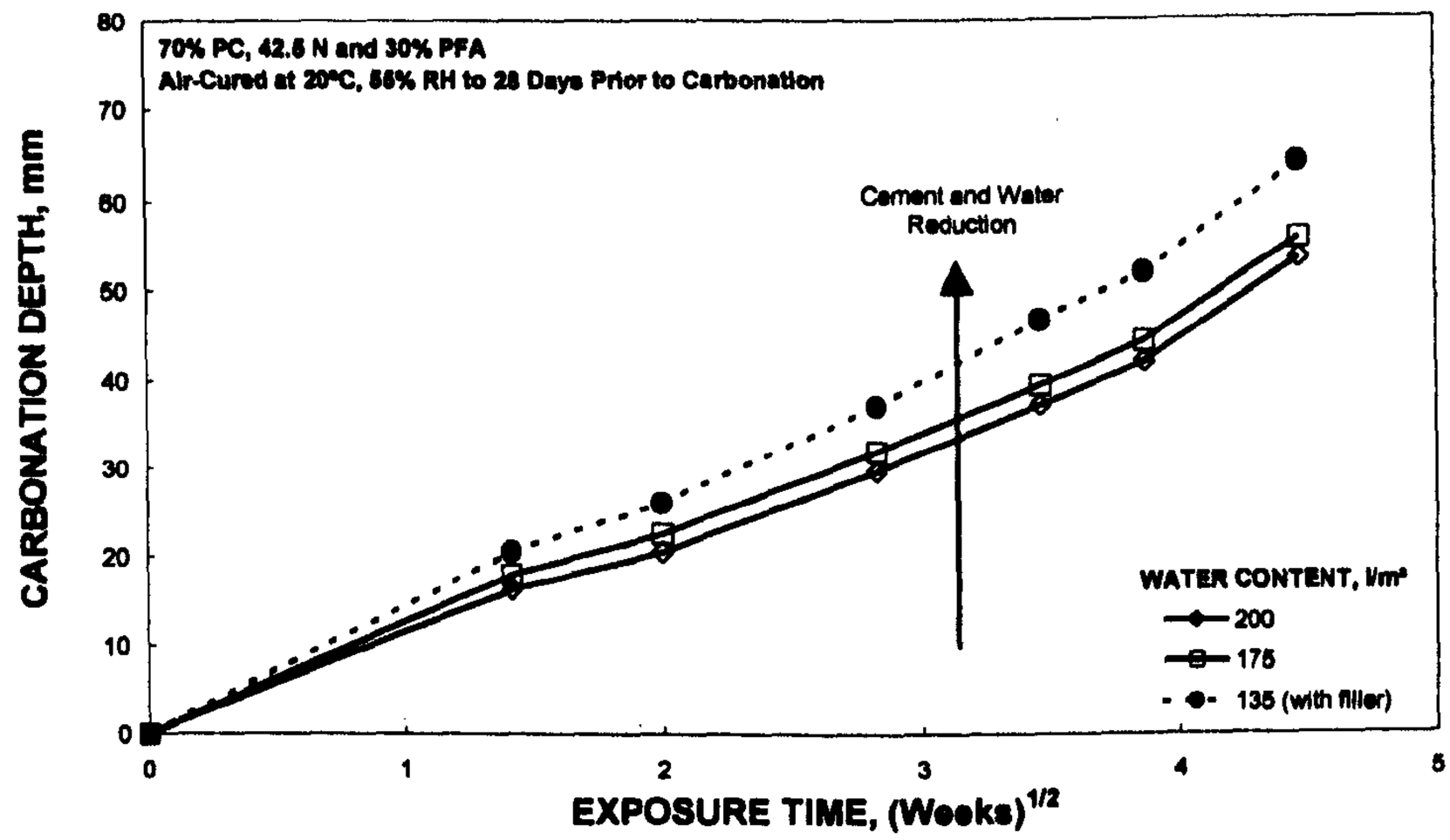


Figure 5.1 (a) Carbonation of concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.55





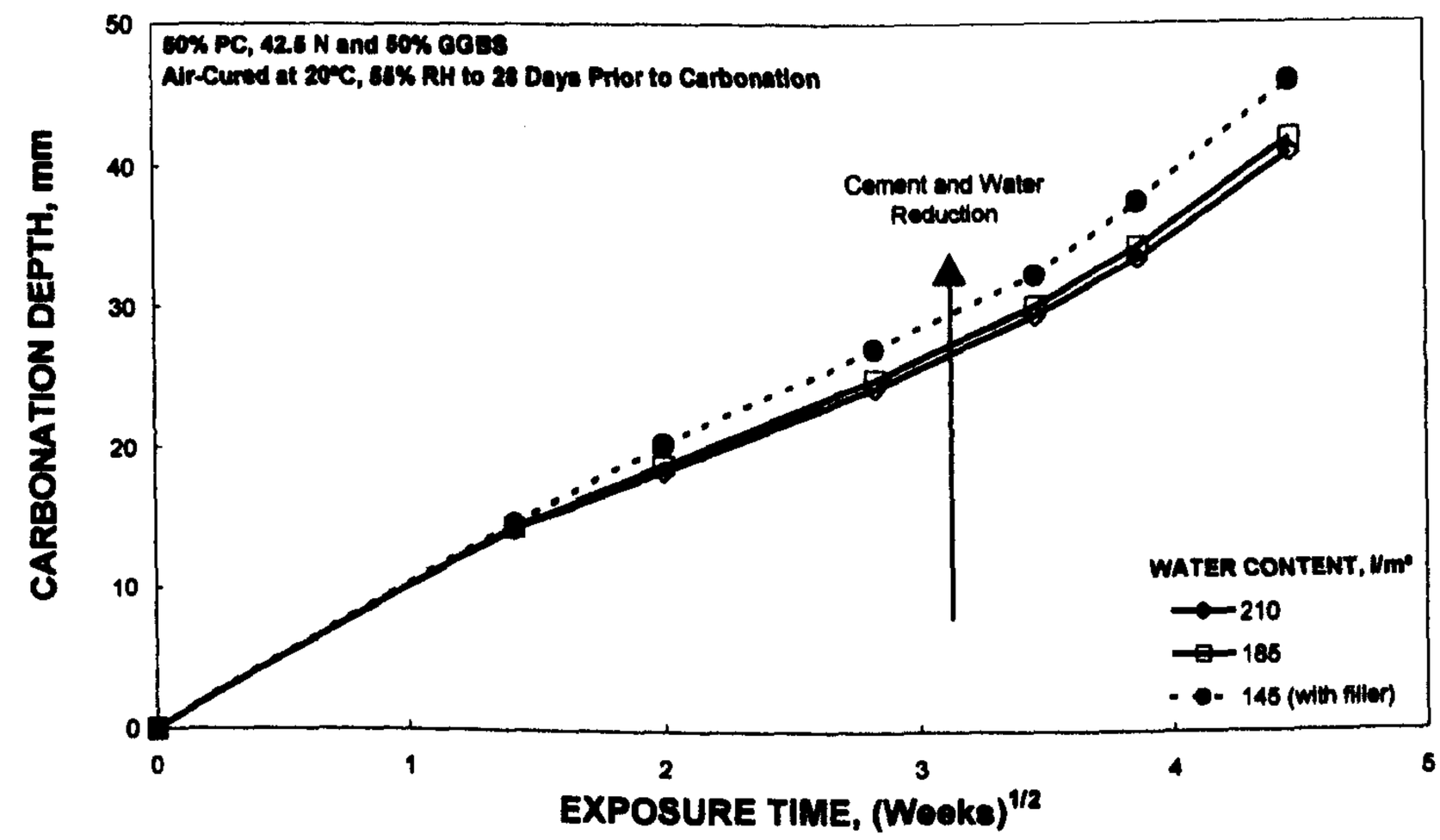


Figure 5.1 (b) Carbonation of concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.55

Table 5.2 Carbonation resistance of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	CARBONATION DEPTH[$] (24 WEEKS)					
		mm			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
	M5*	23.0	19.5	20.0	96	98	93
	M1	24.0	20.0	21.5	100	100	100
0.55	M2*f*[#]	n/t	n/t	28.0	n/t	n/t	130
	M2[#]	n/t	n/t	32.5	n/t	n/t	151
	M3*f*[#]	26.0	21.5	31.5	108	108	147

(b) Made with different cement types

W/C RATIO	MIX	CARBONATION DEPTH[$] (20 WEEKS)					
		mm			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
	M5*	18.5	53.5	41.0	93	96	98
	M1	20.0	56.0	42.0	100	100	100
0.55	M2*f*[#]	26.0	n/t	n/t	130	n/t	n/t
	M2[#]	30.0	n/t	n/t	150	n/t	n/t
	M3*f*[#]	29.0	64.0	46.0	145	114	110

[$] 4.0% CO_2 exposure, 20 ℃, 55% RH
All concrete air cured at 20 ℃, 55% RH to 28 days prior to carbonation
All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

Concrete of Different Coarse Aggregate Types

The results indicate that at w/c ratio 0.55;

- For concrete made with dolomitic magnesium limestone, when cement and water contents were reduced, carbonation depth tended to increase compared to the Reference Mix (M1). This effect was noticeable when the fines content was allowed to deplete. Indeed, Mix M2 resulted in a greater increase in carbonation depth after 24 weeks (51%) compared to the Reference Mix (M1). However, this was partly offset with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix (M1) and, thus, Mixes M2*f* and M3*f* resulted in 30 and 47% increases in final carbonation depth, respectively, compared to the Reference Mix (M1). When cement and water contents were increased with workability increase from

75 to 180 mm nominal slump (M5), carbonation depth after 24 weeks reduced slightly by 7% compared to the Reference Mix (M1).

- The above trends did not change with the use of natural gravel or granite coarse aggregates. However, variation in cement and water contents, particularly cement and water reduction compared to the Reference Mix (M1), had only a minor influence on carbonation depth compared to concrete made with limestone (reduced by up to 4% for Mix M5 and increased by up to 8% for Mix M3*f* in comparison to the Reference Mix (M1), after 24 weeks). In addition, for a given mix, PC / granite concrete showed the highest resistance to carbonation. However, there was no significant difference in carbonation depths at a given time during the exposure between concrete made with natural gravel and dolomitic magnesium limestone.

The controlling mechanisms of carbonation resistance with variation in cement and water contents in equal proportion are likely to be as discussed in Section 4.5.1. Comparison of the results in Tables 5.1 and 5.2 indicates that there was no very strong relationship between the compressive strength and the carbonation resistance of concrete. However, it should be noted that these two tests were carried out using 28-day water-cured and air-cured concrete specimens, respectively. Whilst the compressive strength (see Table 5.1) and concrete microstructure (see Section 4.4) generally improved with cement and water reduction, the observed behaviour indicates that in addition to the concrete microstructure, the pore fluid chemistry associated with the concentration of the alkali is likely to control the carbonation rate, as suggested by Richardson (1988). As stated previously, carbonation rate is mainly influenced by the diffusivity of concrete, which is not necessarily directly related to air permeability or compressive strength (Neville, 1995). It is worth mentioning again, as noted by Buenfeld and Okundi (1998) that the influence of cement and water reduction on oxygen diffusion coefficient was not as high as that on the oxygen permeability in terms of beneficial effects. Therefore, it appears that carbonation resistance of concrete with variation in cement and water contents in equal proportion is likely to be a balance between concrete microstructure and pore fluid chemistry.

Moreover, reduced fines content (which, it is believed to be necessary to achieve a closed structure) and possible increasing in ITZ area, which has the highest porosity of the composite (though reduced bleeding partly offsets this effect), may also contribute to the observed results with cement and water reduction. The slightly better performance when limestone filler was included, compared to the corresponding mix without filler, is probably due to the increased fines content and hence the likelihood of achieving a closed structure. In addition, the inclusion of limestone filler is likely to be further beneficial with improved quality of the cement paste, possibly due to mechanisms discussed earlier (see Section 4.3.1, Compressive Strength), *i.e.* enhanced hydration of cement

particles, improved particle packing, reduced bleeding, chemical reactivity and absorption / adsorption characteristics of limestone filler.

Carbonation of concrete is likely to be increased with aggregate porosity, at a given cement paste porosity, due to the potential increase in diffusion of carbon dioxide through high porosity aggregates (Zhou, 2001). This probably explains the better performance of concrete made with granite coarse aggregates compared to that made with other coarse aggregate types. On the other hand, as stated earlier in Section 4.3.1, cement paste is likely to be absorbed into the aggregates with higher porosity and, in addition, limestone aggregates may react with PC hydration products. Both of these mechanisms may contribute to improve the interface between aggregates and cement paste. This may be a reason for the little differences between concrete made with natural gravel and dolomitic magnesium limestone.

Concrete of Different Cement Types

The influence of variation in cement and water contents in equal proportion on carbonation resistance of concrete was not altered by the use of PFA or GGBS with PC. However, it is worth noting some points observed at w/c ratio 0.55;

- For both PC / PFA and PC / GGBS concrete, variation in cement and water contents, particularly cement and water reduction relative to the Reference Mix (M1), had only a minor influence on carbonation depth compared to PC concrete (reduced by up to 4% for Mix M5 and increased by up to 14% for Mix M3*f* in comparison to the Reference Mix (M1), after 20 weeks). In addition, the effect of cement type on carbonation was more pronounced than the effect of cement content and, thus, both PC / PFA and PC / GGBS concrete showed higher carbonation rates compared to PC concrete and this was highest for PC / PFA.

A review carried out by Parrott (1987) indicates that at a given w/c ratio, the carbonation depth increases compared to PC concrete if PFA or GGBS is used as a cement component. This is probably attributed to the reduced pore fluid alkalinity due to PC replacement and pozzolanic reactions. Therefore, water / PC ratio may be a more universal parameter for describing carbonation when cement combinations are used (Parrott, 1987). In addition, due to slow reacting systems of concrete made with PFA or GGBS, poor curing is likely to affect both microstructure and pore fluid alkalinity of these concrete more than PC concrete. These mechanisms have probably highlighted the effect of cement type on carbonation in comparison to the effect of cement content.

The mechanisms discussed for concrete made with different coarse aggregate types in controlling the carbonation resistance with variation in cement and water contents in equal proportion,

i.e. change in concrete microstructure, pore fluid alkalinity, fines content, ITZ area and improved quality of the cement paste with the use of limestone filler, are applicable to concrete made with different cement types as well. Therefore, it appears that carbonation resistance of concrete made with different cement types with variation in cement and water contents in equal proportion is also a balance between concrete microstructure and pore fluid chemistry.

5.2.2 Carbonation-Induced Corrosion

Figures 5.2 (a) and (b) show the corrosion potential and current measurements against the exposure period to 24 weeks (high humidity environment at 20°C and 95% RH) for concrete made with different coarse aggregate and cement types, respectively. The final corrosion potentials, corrosion currents, calculated corrosion rates and rust indices made by visual assessment of recovered steel after 24 weeks exposure for concrete made with different coarse aggregate and cement types, are given in Tables 5.3 (a) and (b), respectively. The classifications used for visual assessment of recovered steel are given in Table 3.8. The corrosion potentials and currents given in Tables 5.3 (a) and (b), are shown in Figures 5.3 (a) and (b) for concrete made with different coarse aggregate types and in Figures 5.4 (a) and (b) for that made with different cement types, respectively, so that comparisons between different concrete types can be made easily.

When assessing the corrosion activity, depassivation was identified at a corrosion potential of -220 mV for standard silver / silver chloride (Ag / AgCl) reference electrode and a corrosion current of 0.2 $\mu A/cm^2$. Indeed, Figg and Marsden (1984) suggest that there is a 90% risk of active corrosion for more negative corrosion potentials than -220 mV with respect to standard Ag / AgCl reference electrode. The depassivation limit of 0.2 $\mu A/cm^2$ corrosion current has been suggested by Andrade and Page (1986) and Andrade *et al* (1990). It should be noted that these limiting values are related to chloride-induced reinforcement corrosion in concrete. However, it is believed that they can be approximately used for carbonation-induced corrosion as well. Many researchers have used the depassivation limit of 0.2 $\mu A/cm^2$ corrosion current successfully (Constantinou and Scrivener, 1995; Dhir *et al*, 1995; Alonso *et al*, 2000).

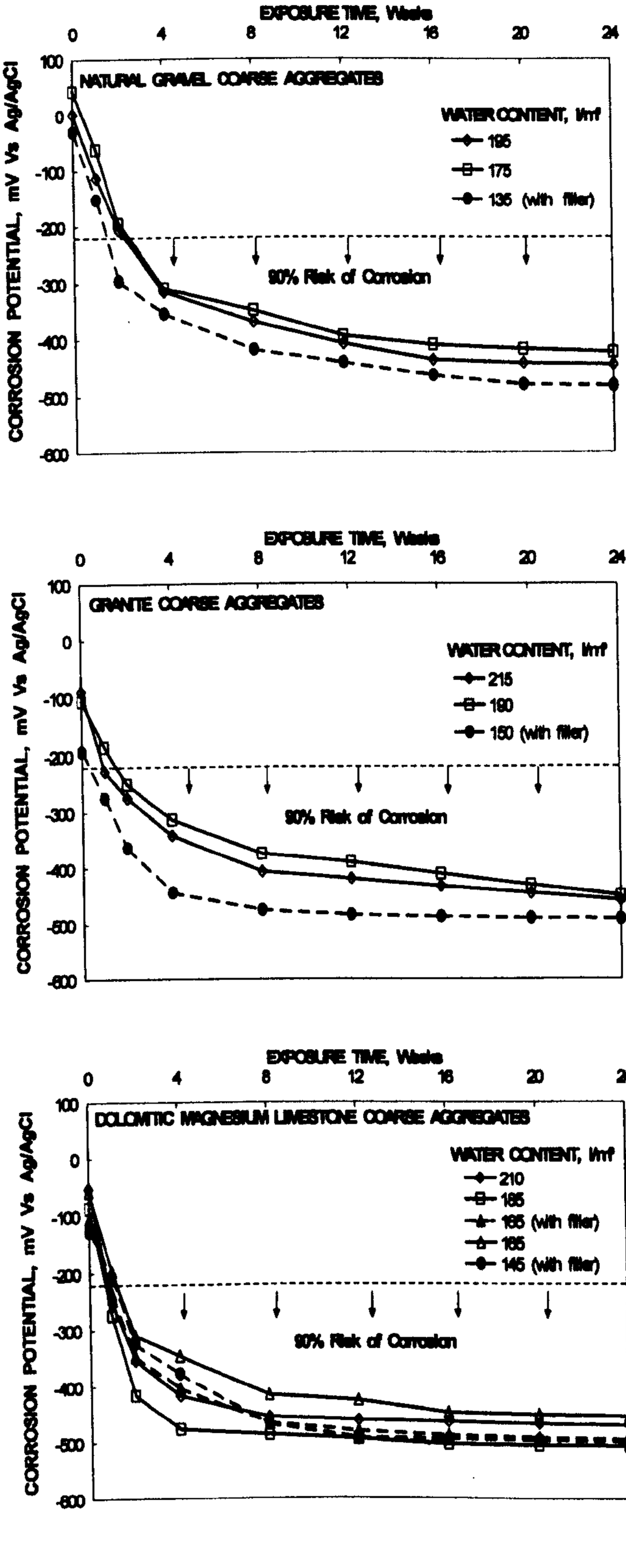
Concrete of Different Coarse Aggregate Types

The corrosion potentials just before exposing to the high humidity environment (after carbonation) varied between +43 and −194 mV and the corrosion currents were between 0.040 and 0.130 $\mu A/cm^2$. Therefore, the resulting corrosion rates varied between 0.5 and 1.5 μm/year. These results suggest that all steel was in a passive state at the beginning of the post-carbonation exposure. Thereafter, negative corrosion potentials and corrosion currents increased gradually with exposure period and reached peak values in about 8 to 16 weeks. After reaching peak values,

corrosion potentials and currents remained approximately the same and, therefore, it was decided to terminate all tests at 24 weeks (see Figure 5.2 (a)). It is worth mentioning that similar corrosion behaviour has been observed by previous researchers (Raphael and Shalon, 1971 cited Parrott, 1987; Dhir *et al*, 1992). The corrosion potentials at the end of the exposure were between –423 and –508 mV. The corrosion currents varied between 0.655 and 0.901 $\mu A/cm^2$ and the corresponding corrosion rates were between 7.5 and 10.5 μm/year (see Table 5.3 (a)). These slight differences between concrete types may be due to variations associated with the carbonation process and corrosion test. The visual examination of recovered steel at the end of the test indicated near uniform corrosion over the bar length for steel from all concrete types. Generally, there was good agreement between the non-destructive test results and the rust indices made by visual assessment of recovered steel when concrete mixes made with a particular aggregate type were considered (see Table 5.3 (a)). It is worth mentioning that similar visual assessment method has been used by Hope and Ip (1987).

As far as the influence of cement content on corrosion is concerned, at a given time, no significant differences in corrosion potentials or corrosion currents (thus, corrosion rates) between steel bars in concrete mixes made with different cement contents were observed (see Table 5.3 (a) for the measured corrosion activities at the end of the exposure period). After 24 weeks exposure, steel in Mixes M6, M1 and M3*f* resulted in corrosion rates of 8.5, 7.5 and 10.0 μm/year and 9.5, 9.0 and 10.5 μm/year for concrete made with natural gravel and granite, respectively. The corrosion rates for steel bars in Mixes M6, M1, M2*f*, M2 and M3*f* of concrete made with dolomitic magnesium limestone were 8.5, 9.5, 8.5, 8.5 and 9.0 μm/year, respectively. These differences are small and can be ignored for practical purposes. In fact, comparable corrosion rates have been observed by previous researchers (Dhir *et al*, 1992; Parrott, 1994; Constantinou and Scrivener, 1995). In addition, the visually assessed rust indices did not show any influence of variation in cement content on corrosion, *i.e.* changing cement content resulted in almost the same rust index for concrete made with a particular aggregate type. Therefore, overall, it can be concluded that at w/c ratio 0.55;

- Reduction in cement and water contents with-or-without the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix (M1), or increasing cement and water contents with workability increase from 75 to 180 mm nominal slump (M5), may have affected carbonation-induced corrosion initiation, but had no influence on subsequent corrosion rates.
- This behaviour was not influenced by the aggregate type used, *i.e.* natural gravel, granite or dolomitic magnesium limestone coarse aggregate. In addition, there was no influence of the aggregate type on carbonation-induced reinforcement corrosion propagation.



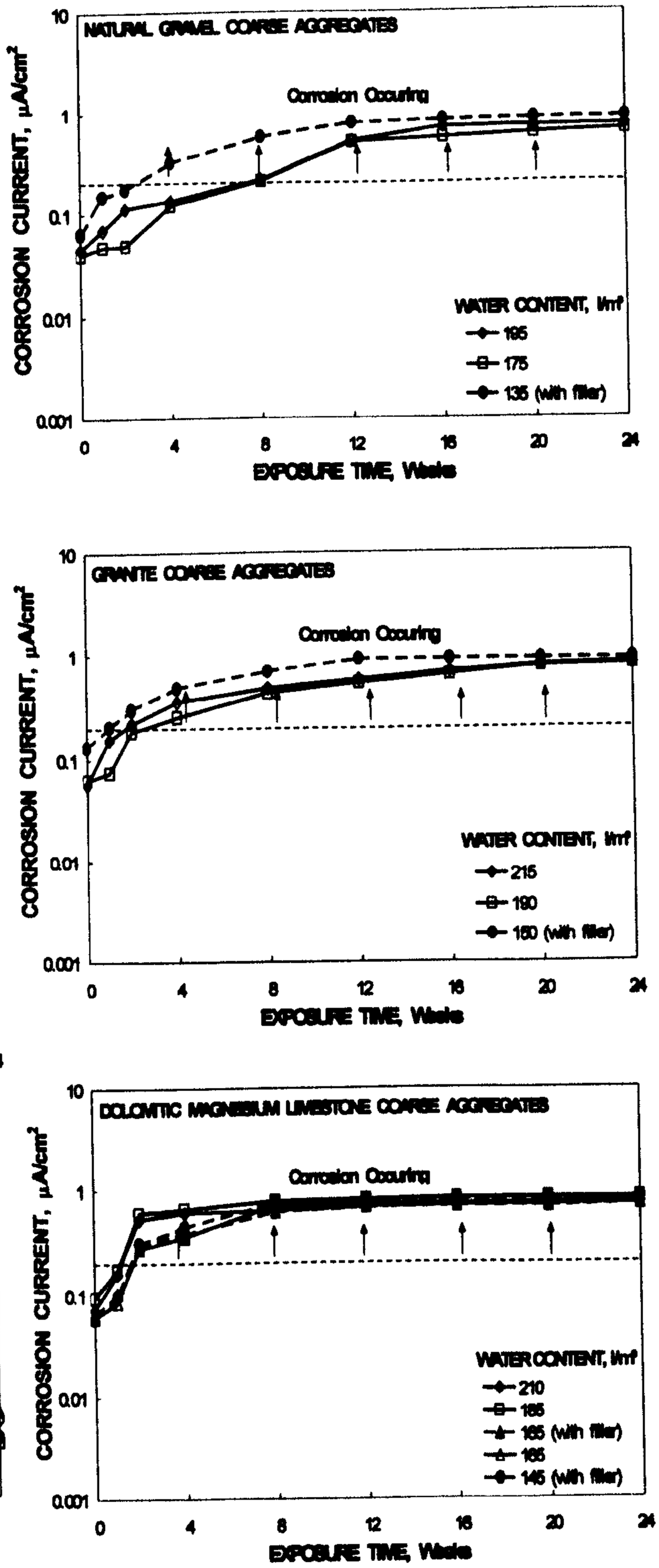
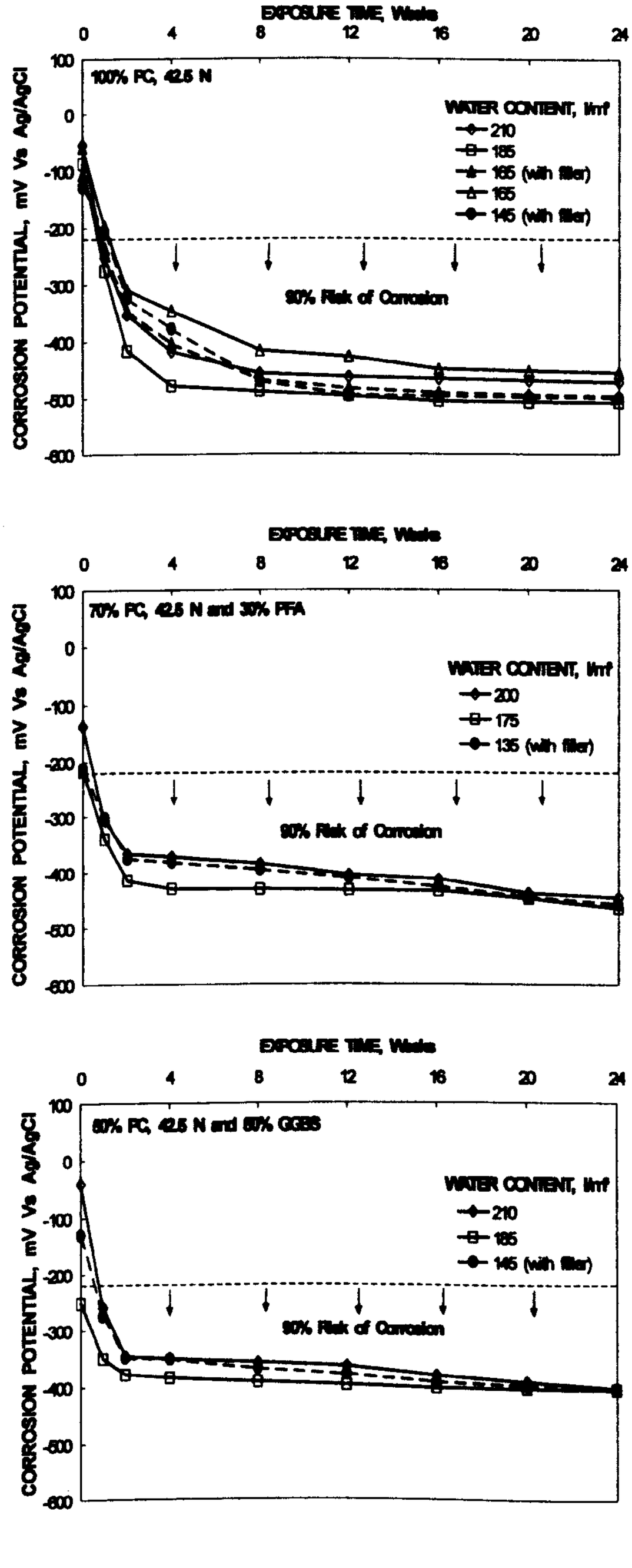


Figure 5.2 (a) Resistance to carbonation-induced reinforcement corrosion of concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.55



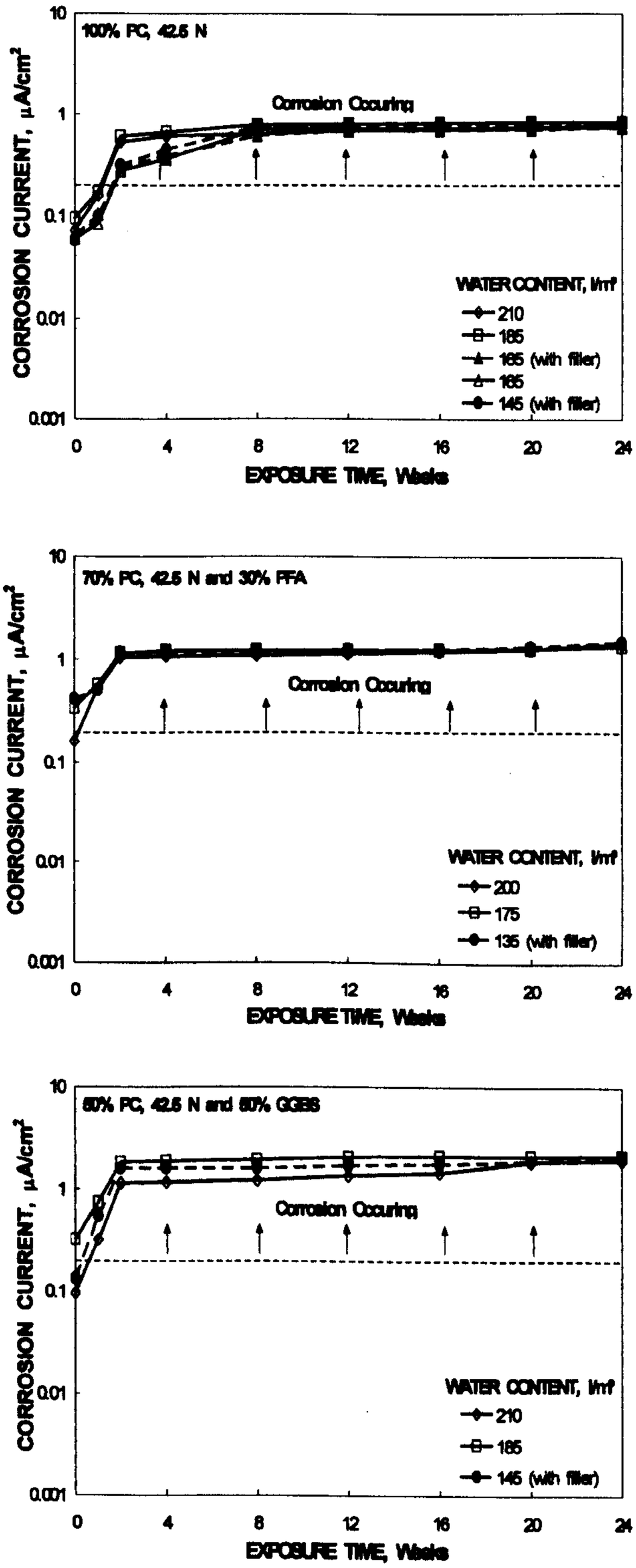


Figure 5.2 (b) Resistance to carbonation-induced reinforcement corrosion of concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.55

Table 5.3 Resistance to carbonation-induced reinforcement corrosion of concrete

(a) Made with different coarse aggregate types

W/C RATIO	COARSE AGGREGATE	MIX	CORROSION DATA[S] (24 WEEKS)			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.55	Natural Gravel	M5*	-445	0.737	8.5	2 to 3
		M1	-423	0.655	7.5	2 to 3
		M3*f*[#]	-483	0.878	10.0	2 to 3
	Granite	M5*	-459	0.814	9.5	2
		M1	-450	0.795	9.0	2
		M3*f*[#]	-492	0.901	10.5	2
	Limestone	M5*	-471	0.734	8.5	2
		M1	-508	0.823	9.5	2
		M2*f*[#]	-496	0.729	8.5	2
		M2[#]	-454	0.749	8.5	2
		M3*f*[#]	-499	0.794	9.0	2 to 3

(b) Made with different cement types

W/C RATIO	CEMENT	MIX	CORROSION DATA[S] (24 WEEKS)			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.55	PC, 42.5 N	M5*	-471	0.734	8.5	2
		M1	-508	0.823	9.5	2
		M2*f*[#]	-496	0.729	8.5	2
		M2[#]	-454	0.749	8.5	2
		M3*f*[#]	-499	0.794	9.0	2 to 3
	PC / PFA	M5*	-446	1.399	16.0	2 to 3
		M1	-464	1.327	15.5	2 to 3
		M3*f*[#]	-457	1.454	17.0	2 to 3
	PC / GGBS	M5*	-402	1.890	22.0	3
		M1	-405	2.084	24.0	3
		M3*f*[#]	-403	1.989	23.0	3

[S] Post-carbonation exposure, 20 ℃, 95% RH
All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Rust index
1: very slight or no corrosion
2: average corrosion
3: moderate corrosion
4: relatively heavy corrosion

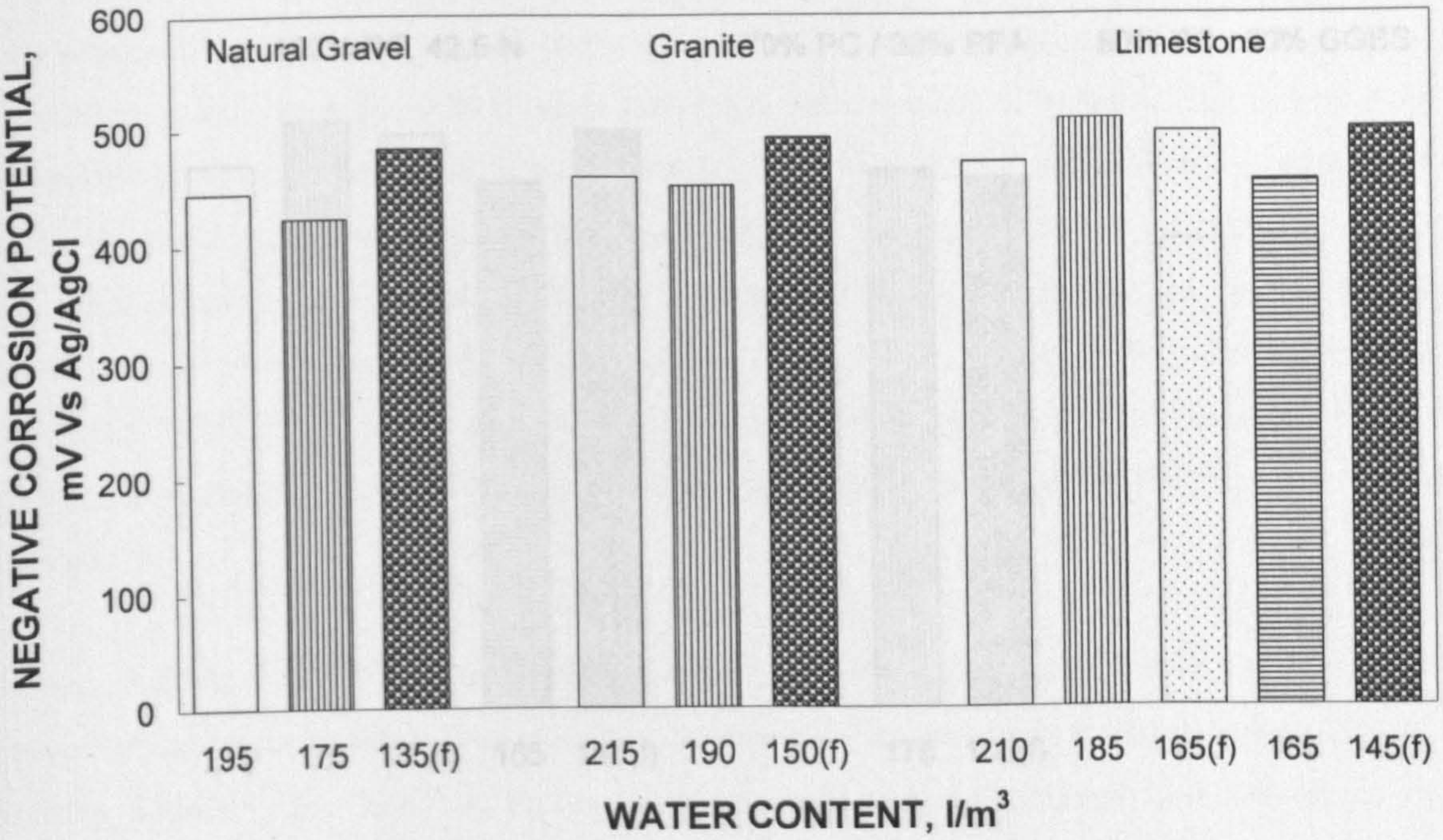


Figure 5.3 (a) Corrosion potentials (24 weeks) of steel in concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.55

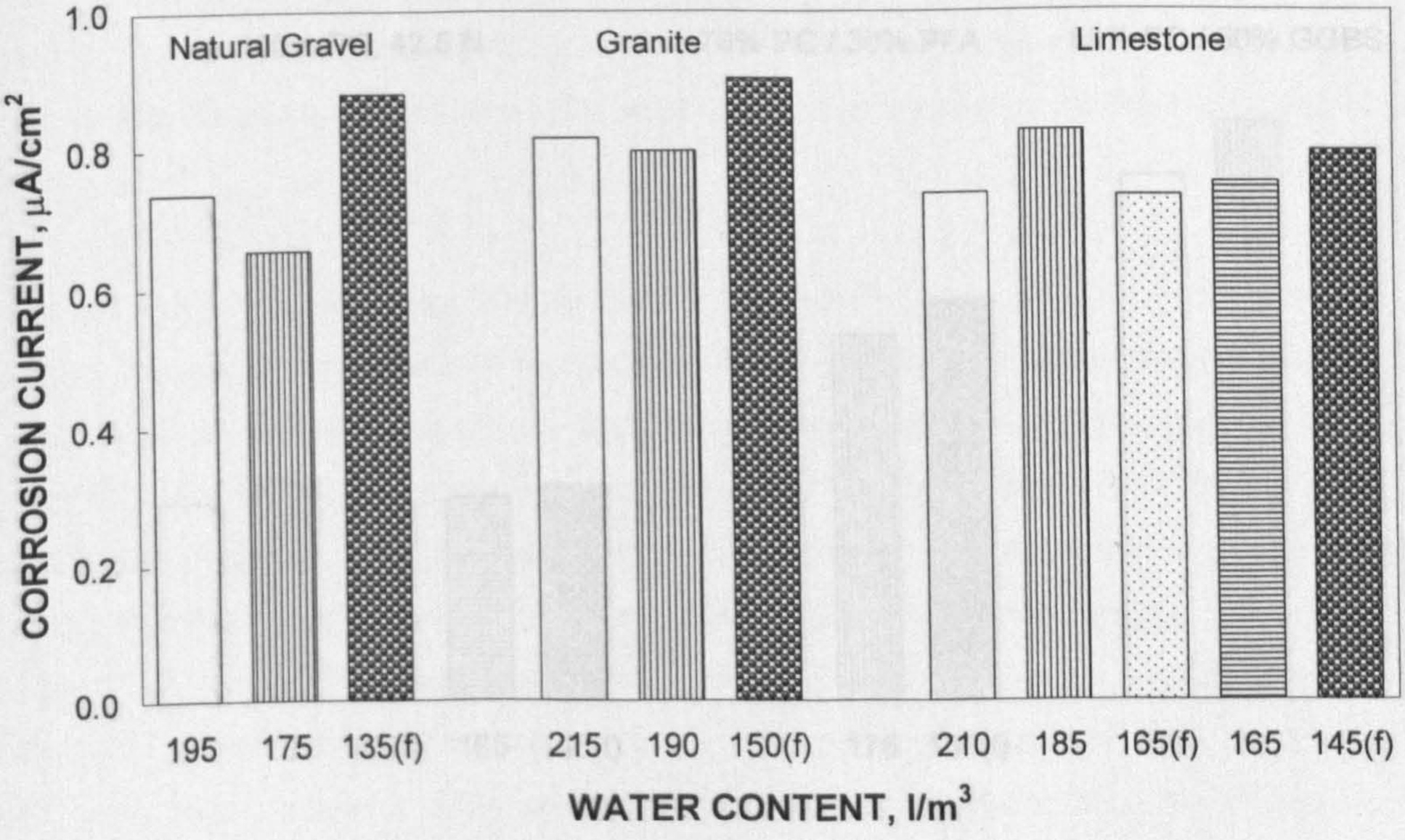


Figure 5.3 (b) Corrosion currents (24 weeks) of steel in concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.55

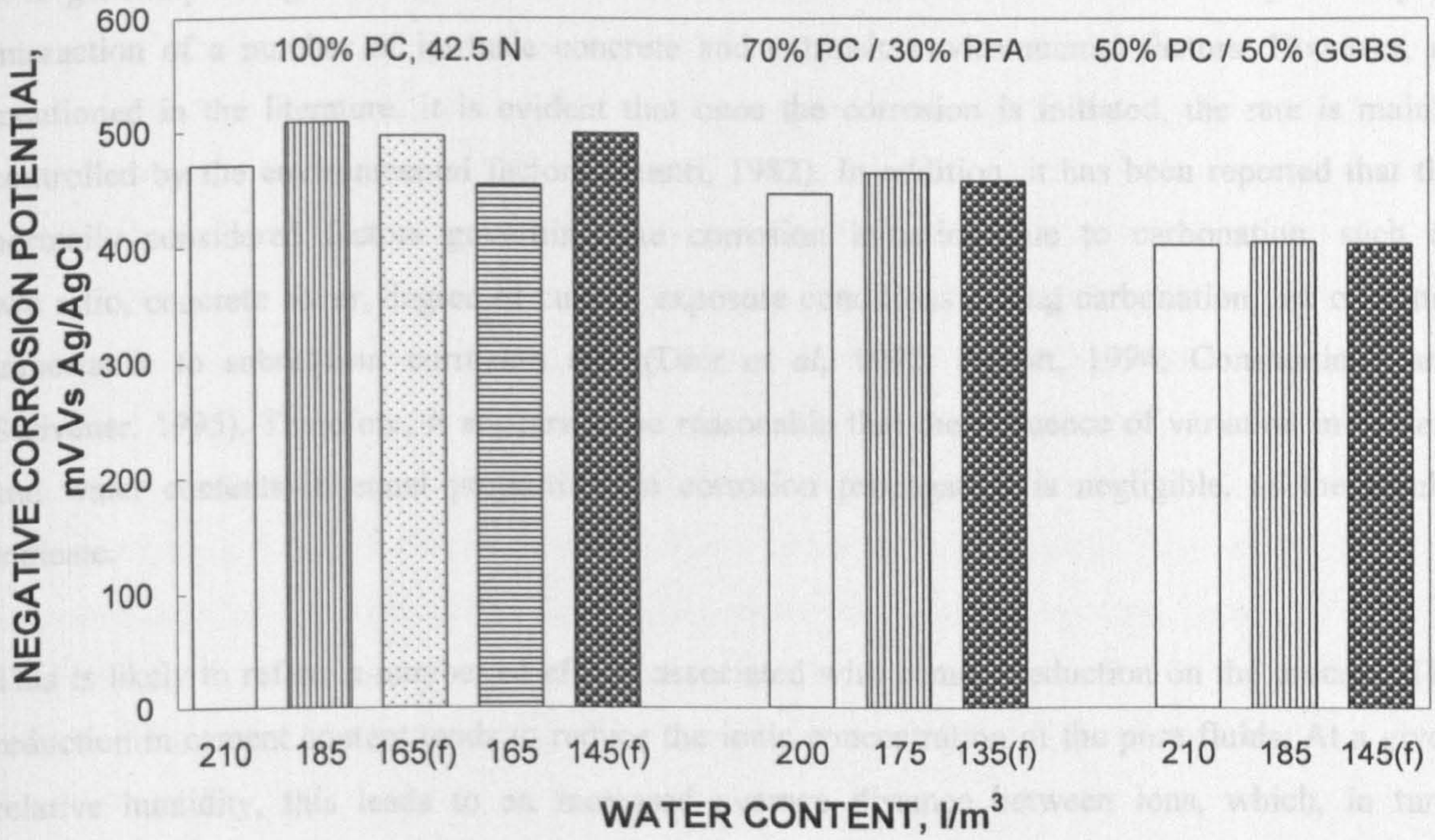


Figure 5.4 (a) Corrosion potentials (24 weeks) of steel in concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.55

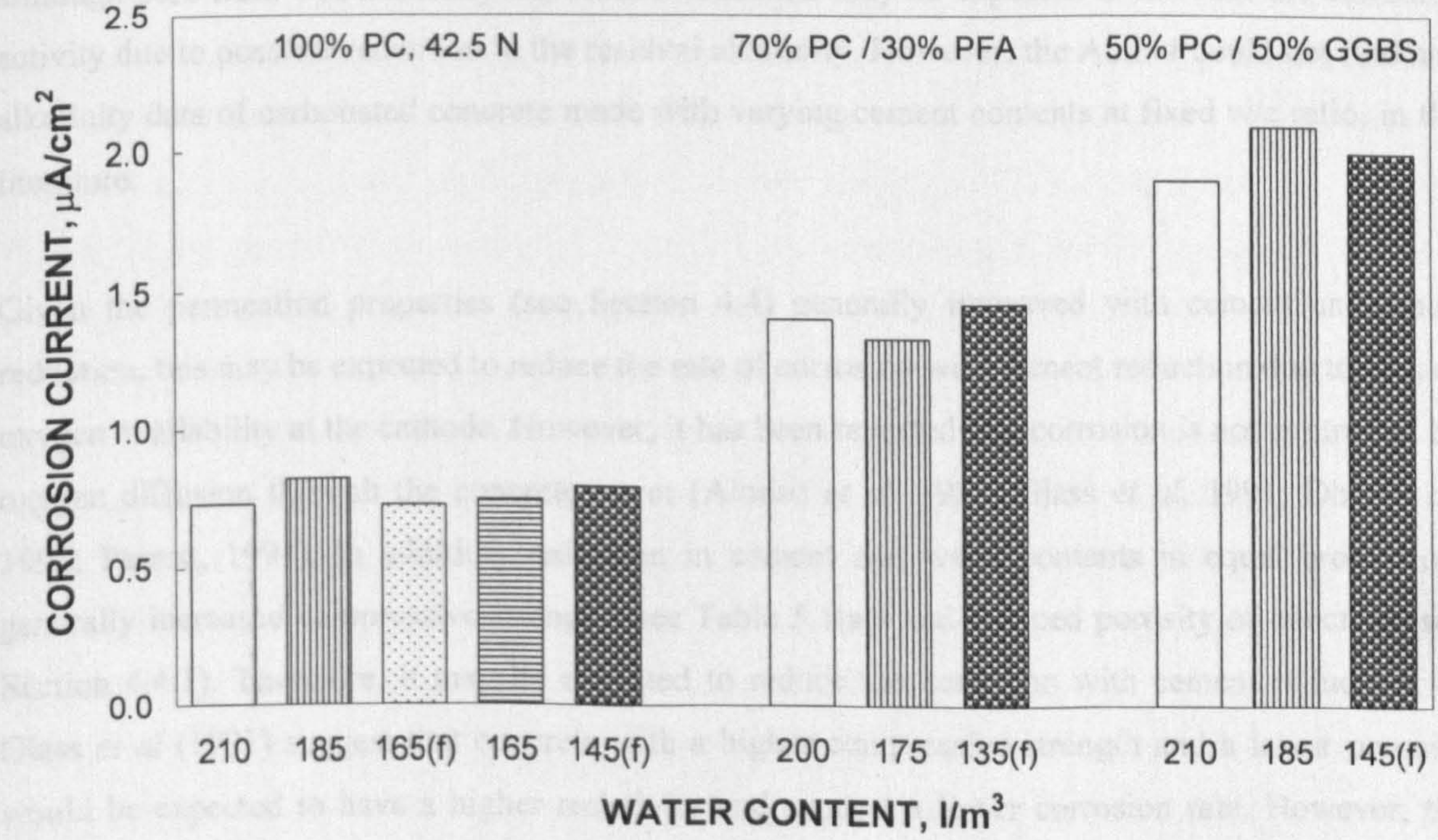


Figure 5.4 (b) Corrosion currents (24 weeks) of steel in concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.55

It is generally thought that the rate of carbonation-induced corrosion is affected by a complex interaction of a number of intrinsic concrete and extrinsic environmental factors. However, as mentioned in the literature, it is evident that once the corrosion is initiated, the rate is mainly controlled by the environmental factors (Tuutti, 1982). In addition, it has been reported that the normally considered factors governing the corrosion initiation due to carbonation, such as w/c ratio, concrete cover, degree of curing, exposure conditions during carbonation, are of minor importance to subsequent corrosion rate (Dhir *et al*, 1992; Parrott, 1994; Constantinou and Scrivener, 1995). Therefore, it appears to be reasonable that the influence of variation in cement and water contents in equal proportion on corrosion propagation is negligible, as the results indicate.

This is likely to reflect a number of effects associated with cement reduction on the process. The reduction in cement content tends to reduce the ionic concentration of the pore fluids. At a given relative humidity, this leads to an increased average distance between ions, which, in turn, increases the ionic mobility. Consequently, the resistance to ionic movement decreases and, therefore, the rate of corrosion may increase.

In addition, as stated in the literature, the residual alkalinity of the pore fluid after carbonation can influence the corrosion rate (Hamada, 1968; Saeki *et al*, 1984, cited Parrott, 1987). Therefore, although pore fluid was not analysed, cement reduction may be expected to increase the corrosion activity due to possible reduction in the residual alkalinity. However, the Author could not find any alkalinity data of carbonated concrete made with varying cement contents at fixed w/c ratio, in the literature.

Given the permeation properties (see Section 4.4) generally improved with cement and water reduction, this may be expected to reduce the rate of corrosion with cement reduction due to lack of oxygen availability at the cathode. However, it has been reported that corrosion is not controlled by oxygen diffusion through the concrete cover (Alonso *et al*, 1988; Glass *et al*, 1991; Dhir *et al*, 1992; Parrott, 1994). In addition, reduction in cement and water contents in equal proportion, generally increased compressive strength (see Table 5.1(a)) and reduced porosity of concrete (see Section 4.4.1). Therefore, it may be expected to reduce the corrosion with cement reduction, as Glass *et al* (1991) suggest that concrete with a higher compressive strength and a lower porosity would be expected to have a higher resistivity and support a lower corrosion rate. However, the observed results suggest that this effect is of minor importance.

In addition, the observed results are likely to be attributed to a number of factors associated with the carbonation process. Parrott (1987) states that carbonation does not necessarily produce sharply

defined reaction fronts and the associated gradients of alkalinity can affect the possible rates of corrosion. Indeed, corrosion is mainly controlled by the unneutralized reminder, *i.e.* the depth of cover minus the depth of carbonation, and the corrosion rate increases as the unneutralized reminder reduces from +5 to –10 mm (Parrott, 1994). Therefore, although it has been mentioned that the method used to measure the carbonation depth using phenolphthalein indicator is accurate and reliable (Broomfield, 1997), it appears that the influence of gradients of alkalinity on the observed results may have become more pronounced than the other possible mechanisms associated with variation in cement content (change in ionic mobility, residual alkalinity, permeation properties and resistivity), as it is not possible to find a clear influence of the cement content on the corrosion rate (see Figure 5.2 (a)). Moreover, this explains why the influence of aggregate type on corrosion activities was not pronounced, despite concrete made with granite showing higher compressive strengths, lower capillary porosities and improved permeation properties compared to that made with other aggregate types (Table 5.1(a) and Section 4.4).

Concrete of Different Cement Types

The variation of corrosion activity with time was essentially similar to that of concrete made with different coarse aggregate types. However, the corrosion potentials just before exposing to high humidity environment (after carbonation) varied between -41 and -253 mV. The corrosion currents were between 0.058 and 0.419 $\mu A/cm^2$ and the resulting corrosion rates were between 0.5 and 5.0 μm/year. This indicates that corrosion was possible at the start of the post-carbonation exposure, particularly for some mixes made with PC / PFA or PC / GGBS (see Figure 5.2 (b)). This is actually not surprising because PC / PFA and PC / GGBS concrete required a shorter time to carbonate to 35 mm depth (approximately 12 weeks for PC / PFA concrete and 15 weeks for PC / GGBS concrete) compared to PC concrete (approximately 30 to 40 weeks) and retained moisture in concrete may have supported corrosion initiation (as concrete may not become completely dry within a short time period). In addition, variations associated with the carbonation process and corrosion test may also have attributed to this. Indeed, this has been observed by previous researchers (Dhir *et al*, 1992; Constantinou and Scrivener, 1995). However, most of the results indicate that steel was in a passive state at the start of the post-carbonation exposure. The peak corrosion potentials and corrosion currents were reached after 8 weeks of high humidity exposure for concrete made with PC, but this took only 2 weeks for concrete made with PC / PFA or PC / GGBS (see Figure 5.2 (b)). The corrosion potentials at the end of the exposure were between –402 and –508 mV. The corrosion currents varied between 0.729 and 2.084 $\mu A/cm^2$ and the corresponding corrosion rates were between 8.5 and 24.0 μm/year. Generally, the visual assessment was in line with the non-destructive test results when concrete mixes made with a particular cement type were considered (see Table 5.3 (b)).

When the influence of cement content on corrosion is considered, at a given time, no significant differences in corrosion potentials or corrosion currents (hence corrosion rates) between steel bars in concrete mixes made with different cement contents were observed (see Table 5.3 (b) for the measured corrosion activities at the end of the exposure period). However, it should be noted that steel in PC / PFA and PC / GGBS concrete showed higher corrosion rates (measured by corrosion currents) compared to PC concrete at all test ages, although this was not reflected by corresponding corrosion potentials. This is because corrosion potential gives an indication of the corrosion risk, not the rate of corrosion (Broomfield, 1997). After 24 weeks exposure, steel in Mixes M6, M1, M2*f*, M2 and M3*f* of concrete made with PC resulted in corrosion rates of 8.5, 9.5, 8.5, 8.5 and 9.0 μm/year, respectively. Steel in Mixes M6, M1 and M3*f* resulted in corrosion rates of 16.0, 15.5 and 17.0 μm/year and 22.0, 24.0 and 23.0 μm/year for concrete made with PC / PFA and PC / GGBS, respectively. These differences are small and can be ignored for practical purposes. Moreover, the visually assessed rust indices indicate that the influence of variation in cement content on corrosion propagation is minor. Therefore, as for the concrete made with different coarse aggregate types, the influence of variation in cement and water contents in equal proportion on resistance of concrete to carbonation-induced corrosion was not altered by the use of PFA or GGBS with PC. However, it is worth noting the following points observed at w/c ratio 0.55;

- The use of PFA or GGBS with PC resulted in higher corrosion rates compared to PC concrete and PC / GGBS concrete resulted in the highest. In addition, the effect of cement content on corrosion rate was insignificant compared to the effect of cement type.

Previous research is in line with the observed results and suggests that generally, the corrosion rate of concrete made with PFA (Dhir *et al*, 1992) or GGBS (Tuutti, 1982; Parrott, 1994) increases compared to PC concrete. This is likely to be attributed to the reduced pore solution alkalinity due to PC replacement and pozzolanic reactions (Parrott, 1987). On the other hand, pozzolanic activities of these cement types tend to reduce marginally the ionic concentration of the pore fluid, particularly calcium ions, increasing the ionic mobility and, consequently, the corrosion activity (Dhir *et al*, 1992). In addition, due to slow reacting systems of concrete made with PFA or GGBS, poor curing may adversely affect the concrete microstructure, resistivity and pore solution alkalinity, resulting in increased corrosion activity compared to PC concrete.

As far as the influence of cement content on corrosion is concerned, the mechanisms controlling corrosion rate with variation in cement and water contents, discussed for concrete made with different coarse aggregate types, are also applicable to concrete made with different cement types. Thus, increased ionic mobility and reduced residual alkalinity (after carbonation) with cement reduction may increase the corrosion rate. On the other hand, increased compressive strength

(see Table 5.1(b)), improved concrete microstructure and reduced porosity (see Section 4.4) with cement reduction may reduce the corrosion rate due to increased resistivity. Therefore, it can be stated that the overall net effect on corrosion may be minor, or the influence of these mechanisms on corrosion rate may be negligible. Moreover, as discussed previously, the variations associated with the carbonation process (associated gradients of alkalinity) may have a pronounced influence on the observed results, as it is not possible to find a clear influence of the cement content on the corrosion rate (see Figure 5.2 (b)).

5.3 CONCLUSIONS

The following conclusions can be drawn from the results in this chapter. Unless otherwise stated, they are based on concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate, *i.e.* the combination of the main cement and aggregate type used for this study. It is worth mentioning again that these conclusions are for air-cured concrete (at 20°C and 55% RH for 28 days) prior to carbonation (4% CO_2 environment at 20°C and 55% RH) and subsequent corrosion propagation (at 20°C, 95% RH). Note that there is a discussion of the practical implications of the work in Chapter 8.

5.3.1 Carbonation Resistance

- When cement and water contents were reduced in equal proportion, carbonation depth tended to be higher than that of the Reference Mix. This effect was notable when the fines content was allowed to deplete, however, this was partly offset with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix. When cement and water contents were increased in equal proportion with workability increase, carbonation depth slightly reduced compared to the Reference Mix.

- These observations were not influenced by the aggregate type. However, the influence of reduction in cement and water contents in equal proportion relative to the Reference Mix, was more pronounced for concrete made with dolomitic magnesium limestone coarse aggregate compared to that made with natural gravel or granite coarse aggregates. In addition, when comparative mixes were considered, concrete made with granite showed the highest resistance to carbonation. However, there were no significant differences in carbonation depths at a given time during the exposure between concrete made with natural gravel and dolomitic magnesium limestone.

- Again, the observations pointed out above were not influenced by the cement type. However, the influence of reduction in cement and water contents in equal proportion relative to the Reference Mix, was more pronounced for concrete made with PC compared to that with

PC / PFA or PC / GGBS. In addition, the effect of cement type on carbonation was more pronounced than the effect of cement content, thus, both PC / PFA and PC / GGBS concrete showed higher carbonation rates compared to PC concrete and this was highest for PC / PFA.

5.3.2 Carbonation-Induced Corrosion

- Reduction in cement and water contents in equal proportion with-or-without the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix, or increasing cement and water contents in equal proportion with workability increase, did not have any influence on subsequent corrosion rates after corrosion initiation.

- This behaviour was not influenced by the aggregate type used in concrete, *i.e.* natural gravel, granite or dolomitic magnesium limestone coarse aggregate.

- Furthermore, the above behaviour was not influenced by the cement type used in concrete. However, both PC / PFA and PC / GGBS concrete resulted in higher corrosion rates compared to PC concrete and PC / GGBS resulted in the highest. In addition, the effect of cement content on corrosion rate was insignificant compared to the effect of cement type.

CHAPTER 6

ROLE OF CEMENT CONTENT ON RESISTANCE OF CONCRETE TO CHLORIDE-INDUCED REINFORCEMENT CORROSION

6.1 INTRODUCTION

The damage to reinforced concrete structures from chloride-induced corrosion, and threat to structural integrity, were discussed earlier, see Sections 2.3.1 and 2.3.3 in the literature review. As far as the role of cement content at fixed w/c ratio on chloride-induced corrosion is concerned, available literature mainly covers chloride ingress, which is the process leading to corrosion initiation (first phase of the overall deterioration process), see Section 2.4.4. Moreover, there are limited data covering the role of cement content on the overall deterioration process (corrosion initiation and propagation), see Section 2.4.5. It is worth reiterating that no particular threshold chloride value for steel corrosion in concrete has been widely accepted and specification or service life prediction using only measured chloride contents or chloride diffusion values, is arguably inappropriate (Mangat and Molloy, 1992; Thomas, 1996). Therefore, the influence of minimum cement content requirements on the resistance of concrete to chloride-induced reinforcement corrosion should be examined and, indeed, this issue has been already raised by a few researchers (Harrison, 1997; Hobbs, 1998; Concrete Society, 1999).

Given this background, the main objective of this study was to examine the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the resistance of concrete to chloride-induced reinforcement corrosion using small-scale, 100 mm cube specimens. The experimental programme of study including concrete mix details, curing details and properties tested, was discussed in Chapter 3 (see Stage 2, chloride-induced corrosion). As mentioned earlier, a range of cement and coarse aggregate combinations was used. PC, 42.5 N, the main cement type, was used with (i) natural gravel, (ii) granite and (iii) dolomitic magnesium limestone. The main coarse aggregate type, dolomitic magnesium limestone, was combined with (i) 100% PC, (ii) 70% PC / 30% PFA and (iii) 50% PC / 50% GGBS. Following the guidelines given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), a w/c ratio of 0.45 was used for all concrete types. The cement content was varied around the minimum cement contents given in these standards. For all specimens, the uppermost surface at casting was selected as the test face because the direction of casting is likely to represent the weakest and, therefore, the critical face in terms of damage to the embedded steel. As described in Section 3.6.5, 28-day water-cured (20°C), reinforced concrete specimens (after preparation) were exposed to cycles of 6 hours wetting with 2 molar (M) sodium chloride (NaCl) solution at 20°C,

followed by 6 hours drying (20°C), together with plain concrete specimens to determine the chloride ion contents after different exposure periods. Monitoring of corrosion was made using corrosion potential and polarisation resistance measurements immediately prior to, and periodically during chloride exposure. After 80 weeks, the cubes were split and a visual assessment was made of the recovered reinforcement. The methods used to assess corrosion (corrosion potential, polarisation resistance and visual condition) and determine chloride contents (total and water-soluble), were discussed in Sections 3.6.6 and 3.6.7, respectively. In addition, chloride diffusion coefficients of all concrete types were determined using the concentration difference (CD) test, as detailed in Section 3.6.4.

It should be noted that the scope of this stage is determining the influence of cement content on resistance of concrete to chloride-induced reinforcement corrosion, not the influence of coarse aggregate and cement type. However, as a range of cement and coarse aggregate types was used, for the convenience of the discussion, the results obtained with concrete made with different coarse aggregate and cement types are presented separately.

6.2. RESULTS AND DISCUSSION

The Reference Mix (M1), the cement-and-water-increased mix with 180 mm nominal slump (M5) and the cement-and-water-reduced (a 40 l/m^3 water reduction) mix with limestone filler (M3*f*) to maintain the fines content equal to that of the Reference Mix (M1), were tested for all aggregate-cement combinations. For the main aggregate-cement combination (*i.e.* dolomitic magnesium limestone and PC), two additional mixes, M2 (a 20 l/m^3 water reduction) and M2*f* (a 20 l/m^3 water reduction with the fines content maintained) were considered to cover an intermediate cement content between Mixes M1 and M3*f*, and to examine the effect of cement reduction with-and-without the maintained fines content.

6.2.1 Chloride Diffusion

The resistance of concrete to chloride diffusion appears to exhibit a close relationship with the compressive strength data (Dhir *et al*, 1987a; Buenfeld and Okundi, 1998). Therefore, it was decided to test all concrete types for compressive strength and Tables 6.1 (a) and (b) give the 28-day compressive strength (water-cured (20°C), 100 mm cube specimens) for concrete made with different coarse aggregate and cement types, respectively. The minor differences between the 28-day compressive strengths of PC / limestone concrete given here and in Section 4.3.1, may be due to variability between batches.

The chloride diffusion coefficients determined using the concentration difference (CD) test method for concrete made with different coarse aggregate and cement types are given in

Tables 6.2 (a) and (b), respectively. Generally, the resistance of concrete to chloride diffusion follows the 28-day compressive strength data. In addition, the influence of cement content on chloride diffusion coefficient is in line with most of the trends given in the literature review (Dhir *et al*, 1987a; Dhir *et al*, 1996; McCarthy *et al*, 1996; Buenfeld and Okundi, 1998).

Table 6.1 Comparison of 28-day compressive strength of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	28-DAY CUBE STRENGTH N/mm²			28-DAY CUBE STRENGTH % of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
0.45	M5*	50.5	55.0	50.0	98	97	100
	M1	51.5	56.5	50.0	100	100	100
	M2*f*#	n/t	n/t	52.5	n/t	n/t	105
	M2#	n/t	n/t	48.0	n/t	n/t	96
	M3*f*#	58.5	65.5	57.0	114	116	114

(b) Made with different cement types

W/C RATIO	MIX	28-DAY CUBE STRENGTH N/mm²			28-DAY CUBE STRENGTH % of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
0.45	M5*	50.0	38.5	41.5	100	94	98
	M1	50.0	41.0	42.5	100	100	100
	M2*f*#	52.5	n/t	n/t	105	n/t	n/t
	M2#	48.0	n/t	n/t	96	n/t	n/t
	M3*f*#	57.0	43.5	49.0	114	106	115

All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

Concrete of Different Coarse Aggregate Types

The results indicate that at w/c ratio 0.45;

- For concrete made with dolomitic magnesium limestone, reduction in cement and water contents led to a slight reduction in chloride diffusion coefficient compared to the Reference Mix (M1). This effect was greatest and most significant when the filler was included to maintain the fines content equal to that of the Reference Mix (M1). Thus, Mix M3*f* resulted in the lowest diffusion coefficient, which was 20% lower than the Reference Mix (M1). Increasing cement and water contents with workability increase from 75 to 180 mm nominal

slump (M5), increased the chloride diffusion coefficient by 8% compared to the Reference Mix (M1).

- The above patterns were not changed by the use of natural gravel or granite coarse aggregates. Thus, for Mix M3*f*, 18 and 11% reductions and, for Mix M5, 8 and 5% increases in chloride diffusion coefficient were observed compared to the Reference Mix (M1) for concrete made with natural gravel and granite coarse aggregates, respectively. In addition, for corresponding mixes, concrete made with granite resulted in the highest resistance to chloride diffusion and that made with dolomitic magnesium limestone the lowest.

Table 6.2 Chloride diffusion coefficient of concrete

(a) Made with different coarse aggregate types

W/C RATIO	MIX	CHLORIDE DIFFUSION COEFFICIENT[S] (CD)					
		$cm^2/s \times 10^{-9}$			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
0.45	M5*	9.2	6.4	10.4	108	105	108
	M1	8.5	6.1	9.6	100	100	100
	M2*f*[#]	n/t	n/t	7.8	n/t	n/t	81
	M2[#]	n/t	n/t	9.4	n/t	n/t	98
	M3*f*[#]	7.0	5.4	7.7	82	89	80

(b) Made with different cement types

W/C RATIO	MIX	CHLORIDE DIFFUSION COEFFICIENT[S] (CD)					
		$cm^2/s \times 10^{-9}$			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
0.45	M5*	10.4	7.2	1.4	108	103	108
	M1	9.6	7.0	1.3	100	100	100
	M2*f*[#]	7.8	n/t	n/t	81	n/t	n/t
	M2[#]	9.4	n/t	n/t	98	n/t	n/t
	M3*f*[#]	7.7	6.0	1.2	80	86	92

[S] 5 M NaCl exposure at 20°C
All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested

As discussed in Section 4.5.2, reduction in cement and water contents in equal proportion is likely to have beneficial and adverse effects on concrete in terms of its resistance to chloride diffusion and, overall, the net effect is due to a combination of these mechanisms.

Ignoring the effects of ITZ, reduction in cement and water contents in equal proportion may result in an increase or a decrease in the concrete's chloride diffusion coefficient, depending on the chloride diffusion coefficient of aggregates and cement paste (Hobbs, 1999). For all concrete types made with different coarse aggregates, as the porosity of the combined aggregate (mainly consisting of coarse aggregate) is lower than that of the cement paste (in concrete), see Section 4.4.1 (capillary porosity), chloride diffusion appears to be mainly through the paste. Thus, the reduced volume of cement paste (and increased aggregate volume) with cement and water reduction might be expected to reduce the diffusion coefficient. Indeed, as stated previously, Hobbs (1999) has shown this theoretically. In addition, reduced diffusion coefficients with cement and water reduction are in line with improved concrete microstructure measured by selected permeation properties (water absorption and ISA–10), see Sections 4.4.2 and 4.4.3. Moreover, greater tortuosity of flow paths with increased aggregate content is likely to reduce the chloride diffusion into the concrete. On the other hand, possible increases in ITZ area (though reduced bleeding partly offsets this effect), reduced fines content (which controls achieving a closed structure) and reduced chloride binding capacity with cement and water reduction, may tend to partly offset the beneficial effects in limiting chloride diffusion. However, as the observed trends indicate, a reduction in chloride diffusion coefficient with reduction in cement and water contents in equal proportion suggest that these adverse effects are less significant.

The inclusion of limestone filler further reduced the chloride diffusion coefficient, probably due to increased fines content and closed structure. In addition, the improved quality of cement paste, possibly due to mechanisms discussed earlier (see Section 4.3.1, Compressive Strength), *i.e.* enhanced hydration of cement particles, improved particle packing, reduced bleeding, chemical reactivity and absorption / adsorption characteristics of limestone filler, is also likely to contribute to this.

The increase in chloride diffusion coefficient with increasing porosity of aggregates for corresponding concrete mixes made with equal cement (and water) contents at fixed w/c ratio, is in line with previous research (Zhou, 2001). This may be due to penetration of chloride ions through high porosity aggregates. On the other hand, as stated earlier in Section 4.3.1, cement paste is likely to be absorbed into aggregates of higher porosity and, in addition, limestone aggregates may react with PC hydration products. Both of these mechanisms may contribute to improve the interface between aggregates and cement paste. However, the results suggest that these mechanisms may not be significant. According to the results, although limestone aggregate (in concrete) has a higher chloride diffusion coefficient compared to other aggregate types, it still appears to be lower than that of the cement paste (in concrete), as cement reduction (decreasing volume of cement paste and increasing volume of aggregate) reduced the diffusion coefficient for all aggregate types.

Concrete of Different Cement Types

The influence of variation in cement and water contents in equal proportion on resistance of concrete to chloride diffusion was not different with the use of PFA or GGBS in cement. Thus, at w/c ratio 0.45;

- The Mix M3*f* resulted in the lowest diffusion coefficients, which were 20, 14 and 8% lower compared to the Reference Mix (M1) for concrete made with PC, PC / PFA and PC / GGBS, respectively. The chloride diffusion coefficients of Mix M5 were the highest and 8, 3 and 8% above the corresponding Reference Mix (M1) for above-mentioned cement types, respectively.
- Both PC / PFA and PC / GGBS concrete showed lower chloride diffusion coefficients than PC concrete and PC / GGBS concrete resulted in significantly lower values. In addition, the effect of cement type on chloride diffusion resistance was more pronounced than that of cement content.

The mechanisms suggested as influencing the behaviour of concrete made with different coarse aggregate types, *i.e.* change in porosity of concrete, tortuosity of flow paths, chloride binding capacity, fines content, ITZ area and improved quality of the cement paste with the use of limestone filler, appear to be applicable to concrete made with different cement types as well, in relation to changes in chloride diffusion coefficient with variation in cement and water contents in equal proportion. The lower chloride diffusion coefficients of concrete containing PC / PFA or PC / GGBS relate to the physical and chemical contributions of these cements to improve the microstructure and chloride binding capacity of concrete (Concrete Society, 1991). Indeed, this behaviour including the best performance of concrete made with PC / GGBS has been observed by many researchers (Leng *et al*, 2000; McCarthy *et al*, 2001). In addition, improvements in the microstructure and chloride binding capacity of concrete containing PC / PFA or PC / GGBS tend to indicate that the cement type is more important than the cement content in governing the resistance of concrete to chloride diffusion. Indeed, this conclusion is in agreement with the results of Dhir *et al* (1996) and Buenfeld and Okundi (1998).

6.2.2 Chloride Content at Cover Depth

The build-up of water-soluble and total chlorides of the concrete at the level of the steel (25 mm cover depth) during the salt wet / dry exposure, followed the expected behaviour with chloride content increasing with exposure period but at a reducing rate. Indeed, similar behaviour has been observed in previous studies (Dhir *et al*, 1995; McCarthy *et al*, 2001). It should be noted that two other samples were taken at 15 and 35 mm depths (for selected concrete mixes) to check the accuracy of the chloride content measurements at 25 mm cover depth (both total and water-soluble). Indeed, the chloride contents at 25 mm cover depth were in between those at 15 and 35 mm depths.

Before discussing the effect of variation in cement and water contents in equal proportion on the development of chloride content, it is worth noting the observed relationships between total and water-soluble chloride contents (Figure 6.1). This represents all the measured chloride contents at the level of the steel during exposure and indicates a near-linear relationship between the total and water-soluble chloride contents. In addition, it demonstrates that approximately 36% of total chlorides are soluble in water. This appears to be acceptable as the free chloride content can vary from about 50% to as low as 20% of the total chloride content (Neville, 1995). As there is a near-linear relationship between the total and water-soluble chloride contents and corrosion is influenced by free chloride ions in the pore solution, it is likely that water-soluble chlorides provide a better indication of those chlorides that are available for corrosion. Therefore, only measured water-soluble chloride contents at the level of the steel are presented in the remainder of this chapter.

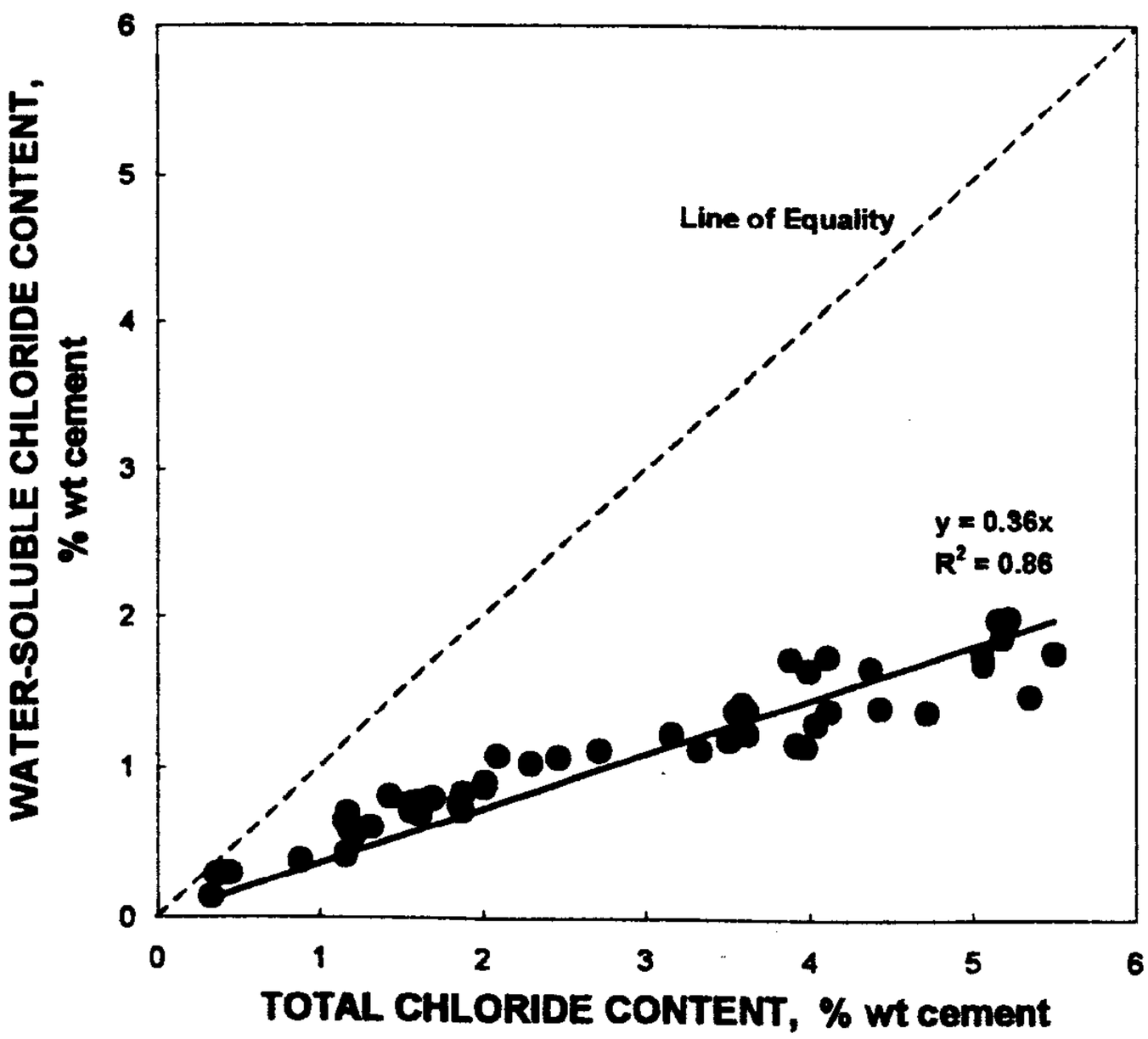


Figure 6.1 Relationship between total and water-soluble chloride contents at the level of the steel

Figures 6.2 (a) and (b) show the water-soluble chloride contents at the level of the steel (taken up to 80 weeks) plotted against exposure period (6 hours wet / dry with 2 M NaCl solution at 20°C) for concrete with different coarse aggregate and cement types, respectively. The final water-soluble chloride contents measured from reinforced concrete specimens at the end of the exposure (after 80 weeks), are given in Tables 6.3 (a) and (b) for concrete made with different coarse aggregate and cement types, respectively. These values vary between 0.83 and 2.01% by weight of cement,

indicating potential for corrosion activity. Indeed, Alonso *et al* (2000) suggest that water-soluble chloride threshold can vary between 0.14 and 1.15% by weight of cement.

As expected, the water-soluble chloride contents were generally in agreement with the chloride diffusion coefficients in terms of ranking with respect to the influence of cement content. It should be noted that the limited chloride content measurement data given in the literature are scattered and do not show a clear influence of cement content on chloride penetration and, therefore, the observed trends cannot be easily related to them. In addition, it is worth mentioning that when the chloride ion content is expressed as a percentage of the weight of cement, cement and water reduced mixes are likely to show higher chloride contents due to their low cement contents.

Table 6.3 Resistance to chloride penetration of concrete

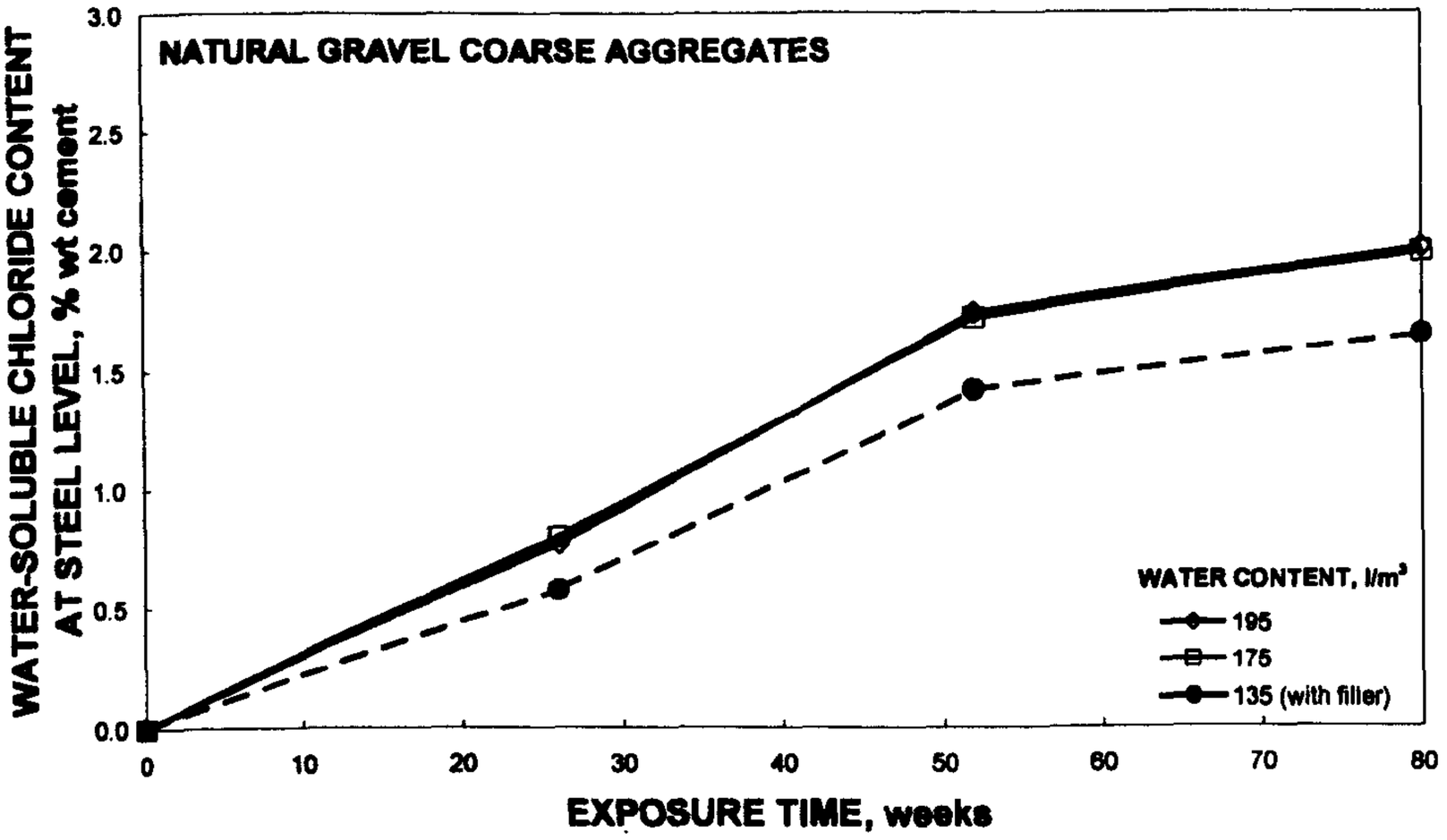
(a) Made with different coarse aggregate types

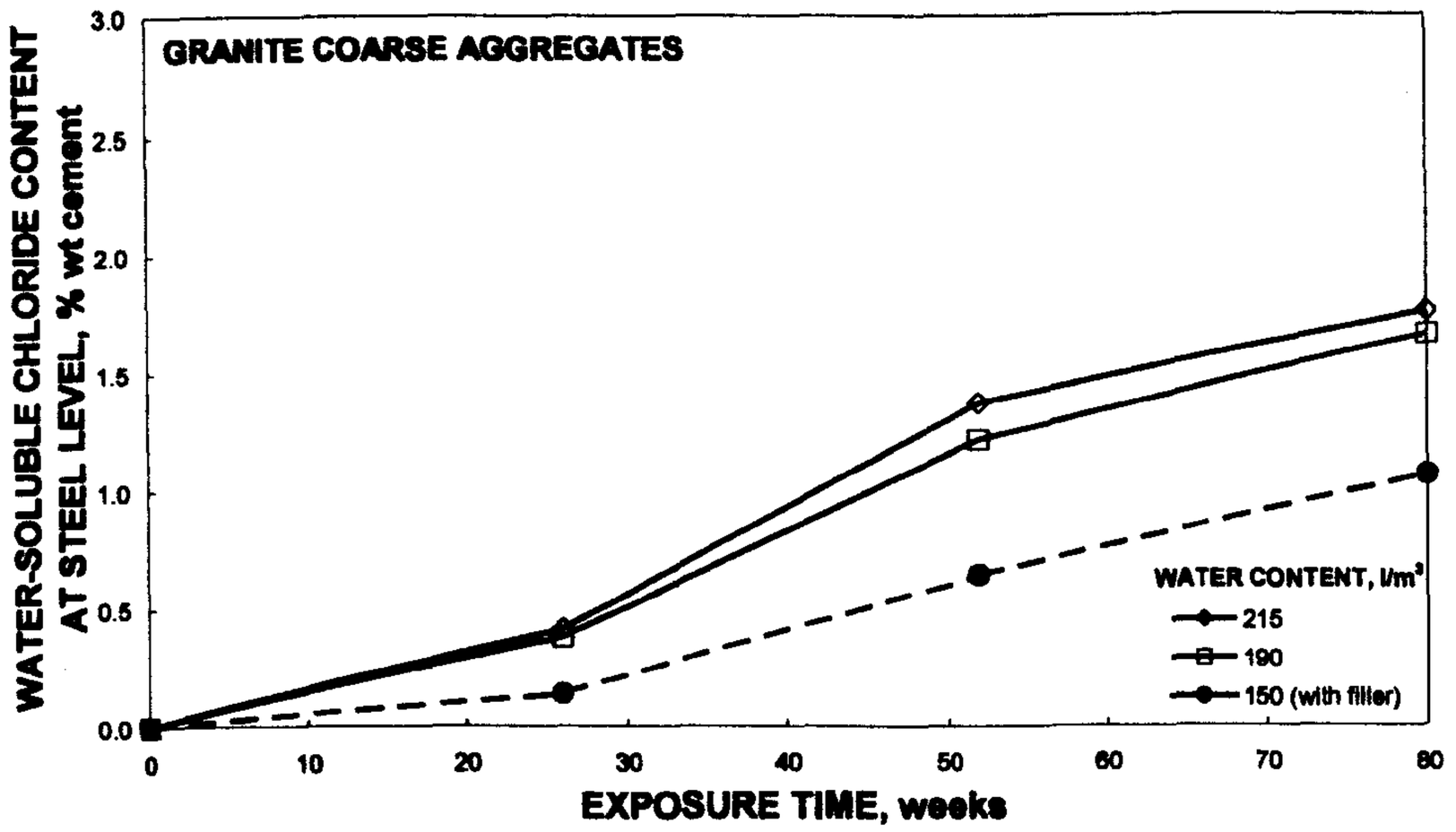
W/C RATIO	MIX	WATER-SOLUBLE CHLORIDE CONTENT AT STEEL LEVEL[$] (80 WEEKS)					
		% by weight of cement			% of M1		
		Natural Gravel	Granite	Limestone	Natural Gravel	Granite	Limestone
	M5*	2.01	1.76	1.86	101	105	105
	M1	1.99	1.67	1.77	100	100	100
0.45	M2*f*[#]	n/t	n/t	1.23	n/t	n/t	69
	M2[#]	n/t	n/t	1.69	n/t	n/t	95
	M3*f*[#]	1.64	1.07	1.38	82	64	80

(b) Made with different cement types

W/C RATIO	MIX	WATER-SOLUBLE CHLORIDE CONTENT AT STEEL LEVEL[$] (80 WEEKS)					
		% by weight of cement			% of M1		
		PC, 42.5 N	PC / PFA	PC / GGBS	PC, 42.5 N	PC / PFA	PC / GGBS
	M5*	1.86	1.38	0.89	105	107	87
	M1	1.77	1.29	1.02	100	100	100
0.45	M2*f*[#]	1.23	n/t	n/t	69	n/t	n/t
	M2[#]	1.69	n/t	n/t	95	n/t	n/t
	M3*f*[#]	1.38	1.11	0.83	80	86	81

[$] 6 hours wet (2 M NaCl solution at 20°C) / dry (20°C) exposure
All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1
n/t Not tested





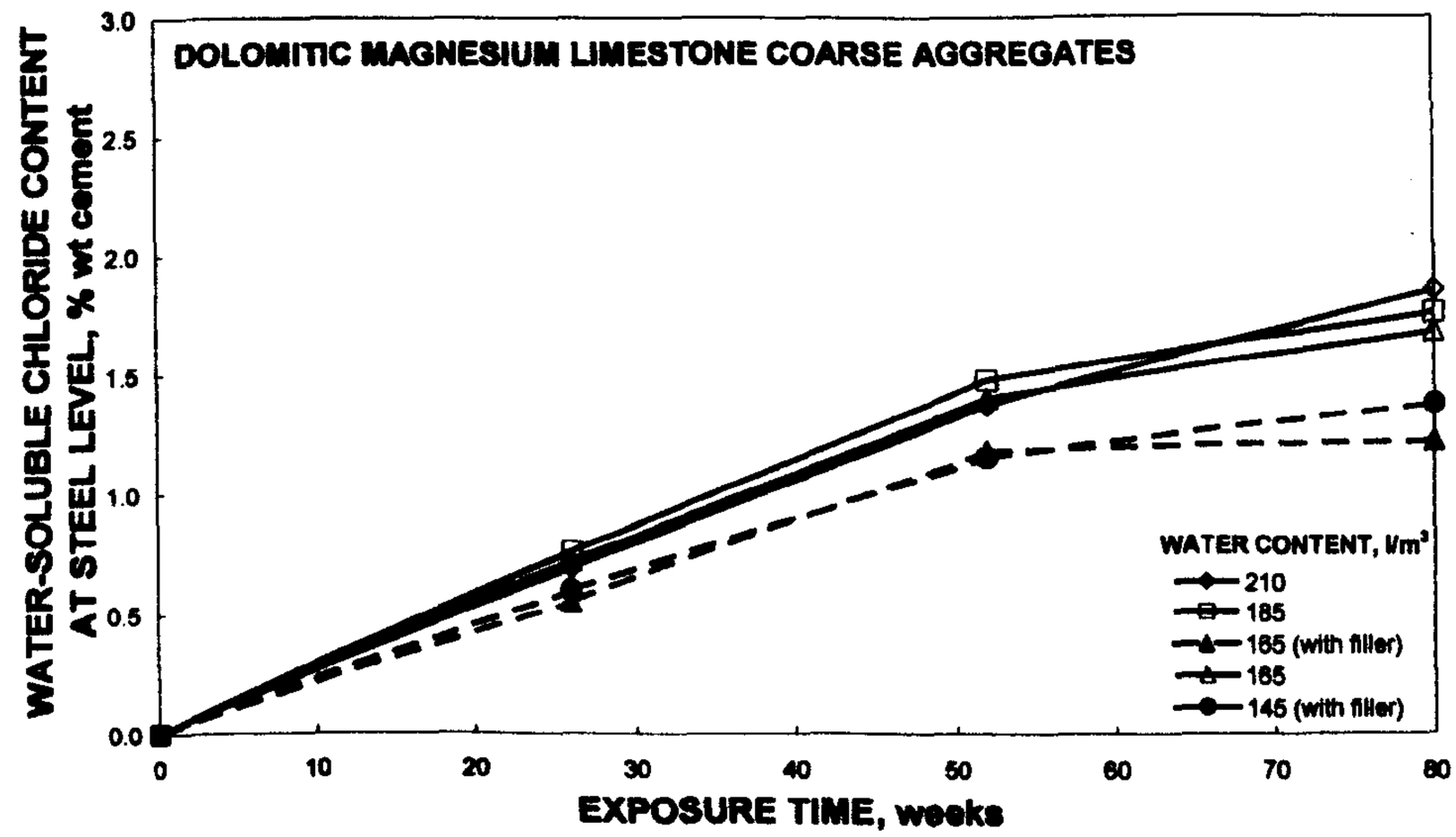
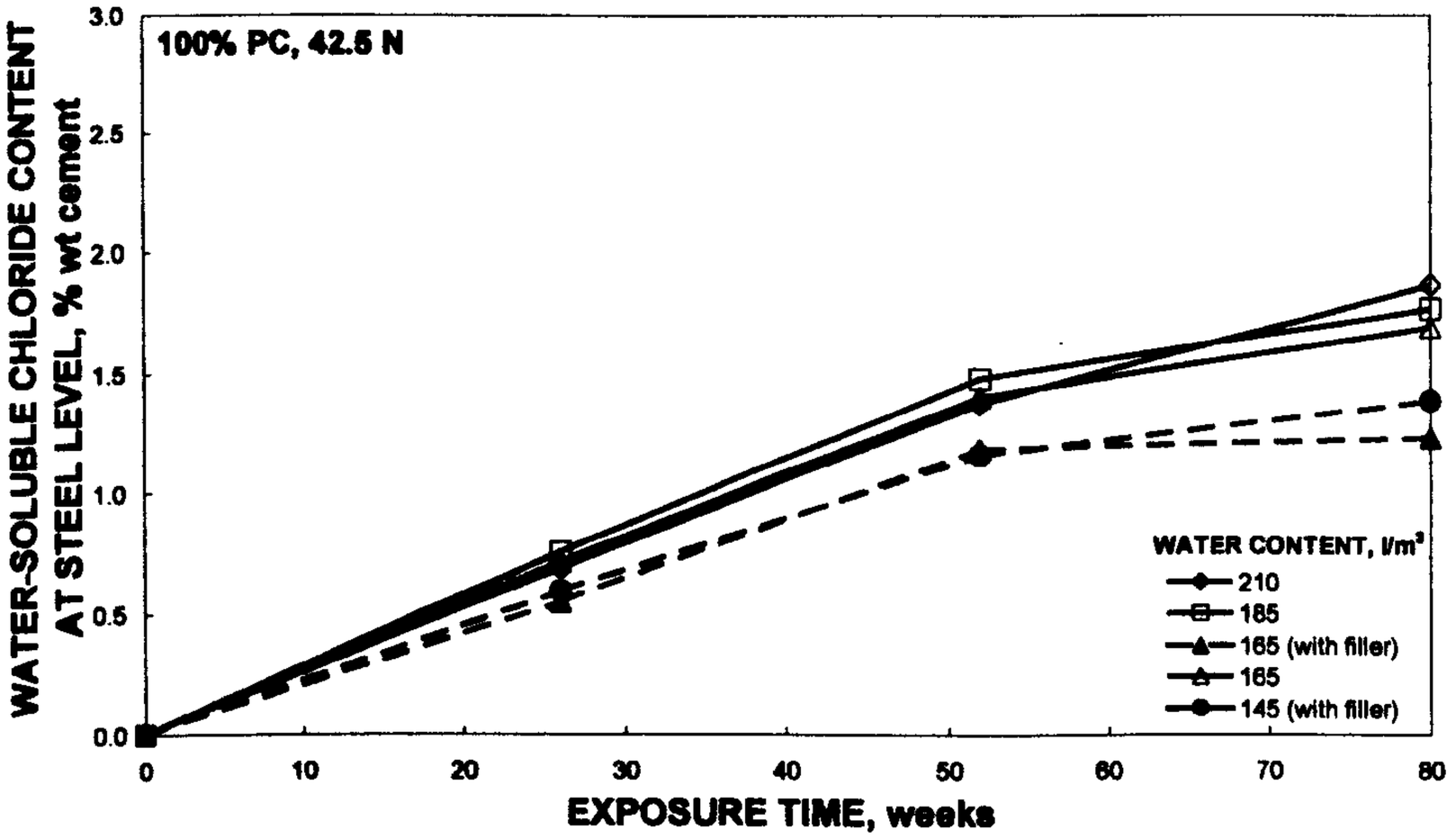
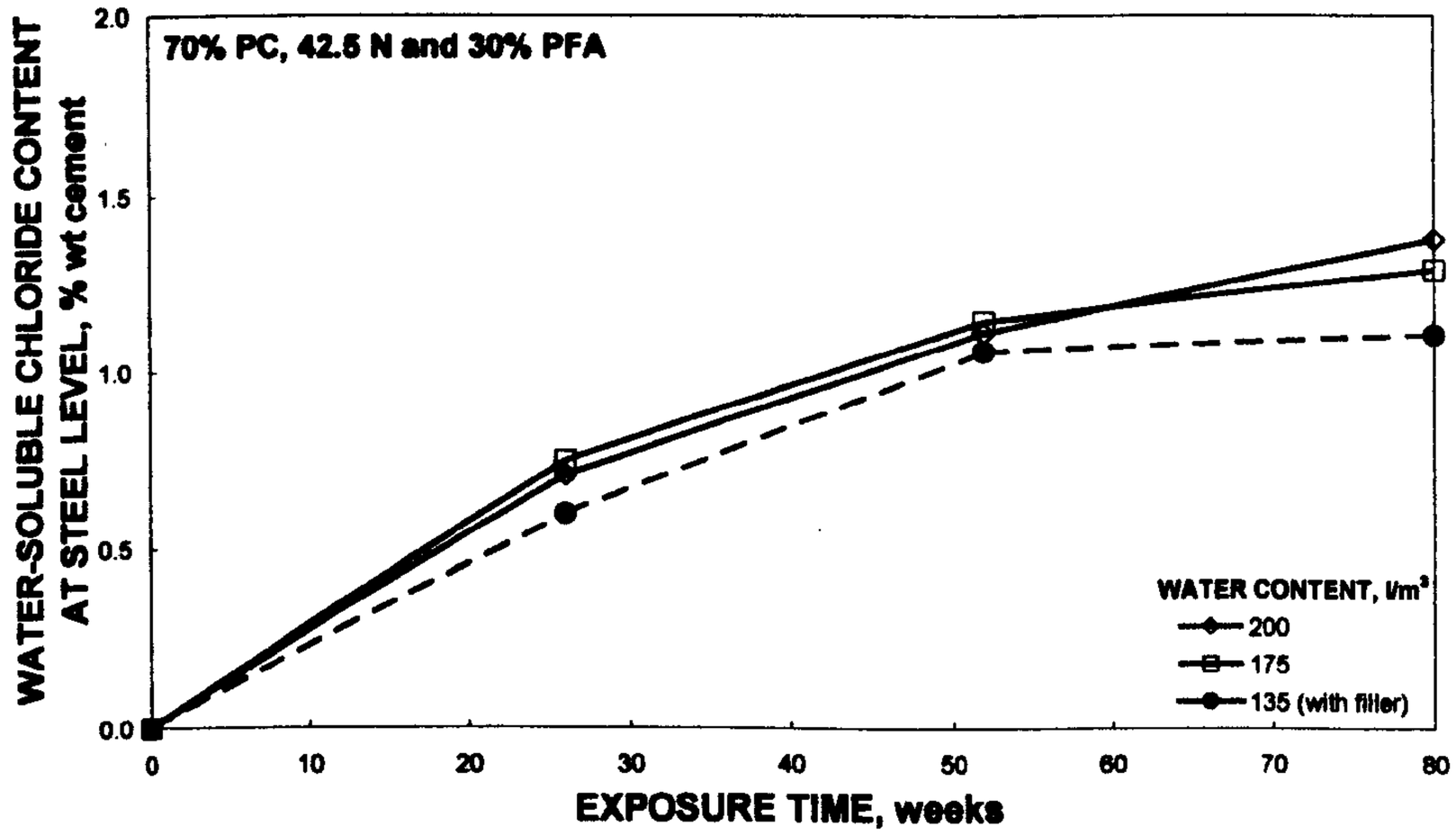


Figure 6.2 (a) Resistance to chloride penetration of concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.45





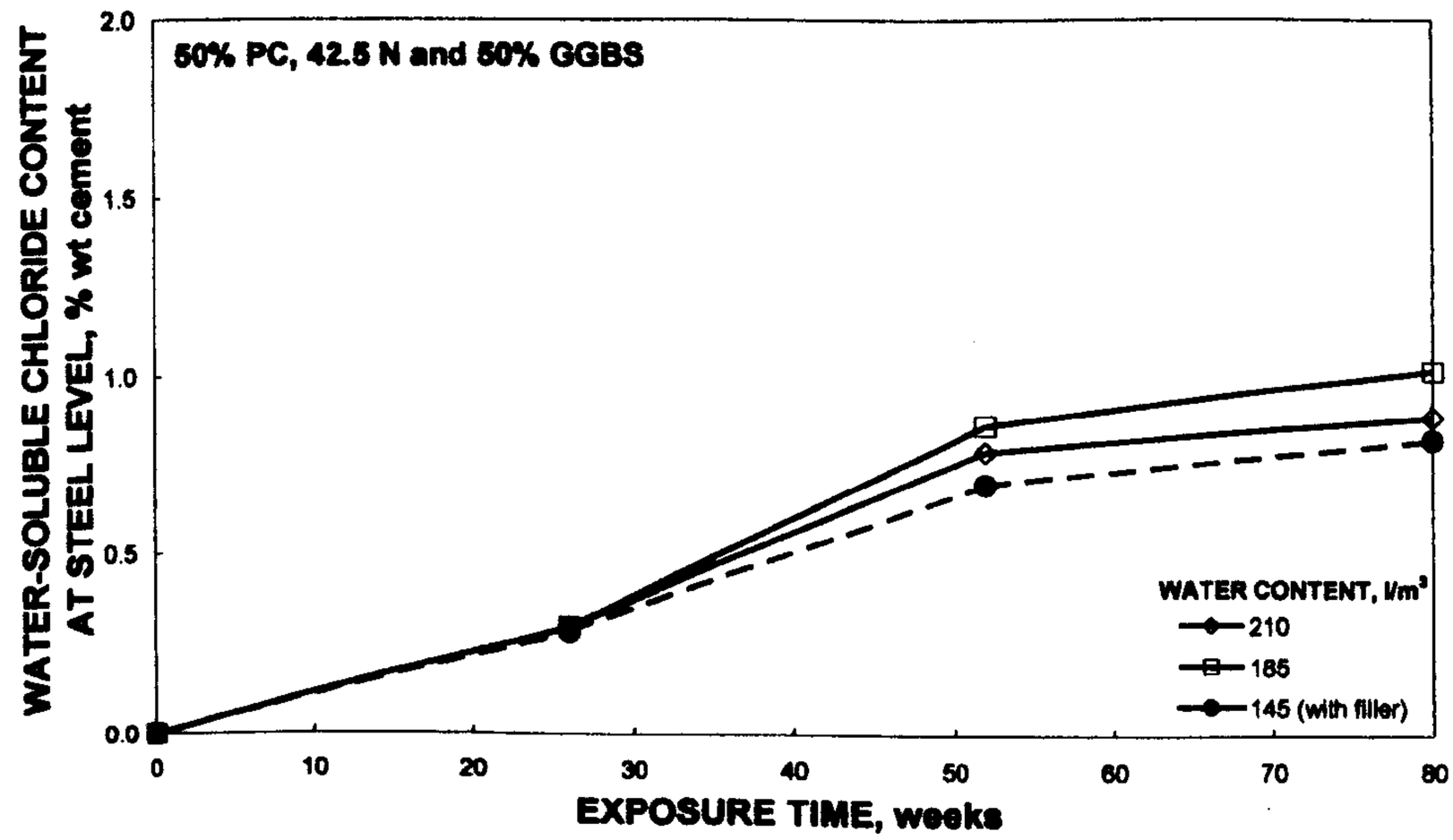


Figure 6.2 (b) Resistance to chloride penetration of concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.45

Concrete of Different Coarse Aggregate Types

It appears that at w/c ratio 0.45;

- For concrete made with dolomitic magnesium limestone, reduction in cement and water contents without the inclusion of limestone filler resulted in a slightly lower chloride content at a given time during the exposure compared to the Reference Mix (M1). However, when the filler was included to maintain the fines content equal to that of the Reference Mix (M1), significantly lower chloride contents were found. Thus, Mixes M2, M2*f* and M3*f* resulted in 5, 31 and 20% reductions in chloride contents, respectively, compared to the Reference Mix (M1), after 80 weeks exposure. Increasing cement and water contents with workability increase from 75 to 180 mm nominal slump (M5), resulted in an insignificant change or only a minor increase in chloride content at a given time compared to the Reference Mix (M1) and the final value was 5% higher.
- The above observations were not changed for concrete made with natural gravel or granite coarse aggregates. Thus, for Mix M3*f*, 18 and 36% reductions and, for Mix M5, 1 and 5% increases in chloride contents were observed (after 80 weeks) in comparison to the Reference Mix (M1) for concrete made with natural gravel and granite coarse aggregates, respectively. In addition, when corresponding mixes were compared, PC / granite concrete showed the highest resistance to chloride penetration. However, there were no significant differences in chloride contents at a given time during the exposure between concrete made with natural gravel and dolomitic magnesium limestone.

The mechanisms associated with variation in cement and water contents in equal proportion to control the chloride diffusion coefficient, *i.e.* change in porosity of concrete, tortuosity of flow paths, chloride binding capacity, fines content, ITZ area and improved quality of the cement paste with the use of limestone filler, are also likely to control the chloride content measurements. Again, comparison of concrete made with granite and other coarse aggregates indicates that some chloride ions are likely to penetrate through high porosity aggregates as well as the surrounding cement paste. The minor differences between concrete made with natural gravel and dolomitic magnesium limestone coarse aggregate may be due to limestone's ability to react with PC hydration products and absorb comparatively higher amounts of cement paste into its pores, improving the interface between aggregates and cement paste.

Concrete of Different Cement Types

In general, the influence of variation in cement and water contents in equal proportion on chloride content at a given exposure was not changed by the use of PFA or GGBS. Thus, at w/c ratio 0.45;

- The Mix M3*f* resulted in 20, 14 and 19% reductions in chloride contents (after 80 weeks) compared to the Reference Mix (M1) for concrete made with PC, PC / PFA and PC / GGBS,

respectively. After 80 weeks exposure, the chloride contents of the Mix M5 were 5 and 7% higher and 13% lower compared to the Reference Mix (M1) for the above cement types, respectively.

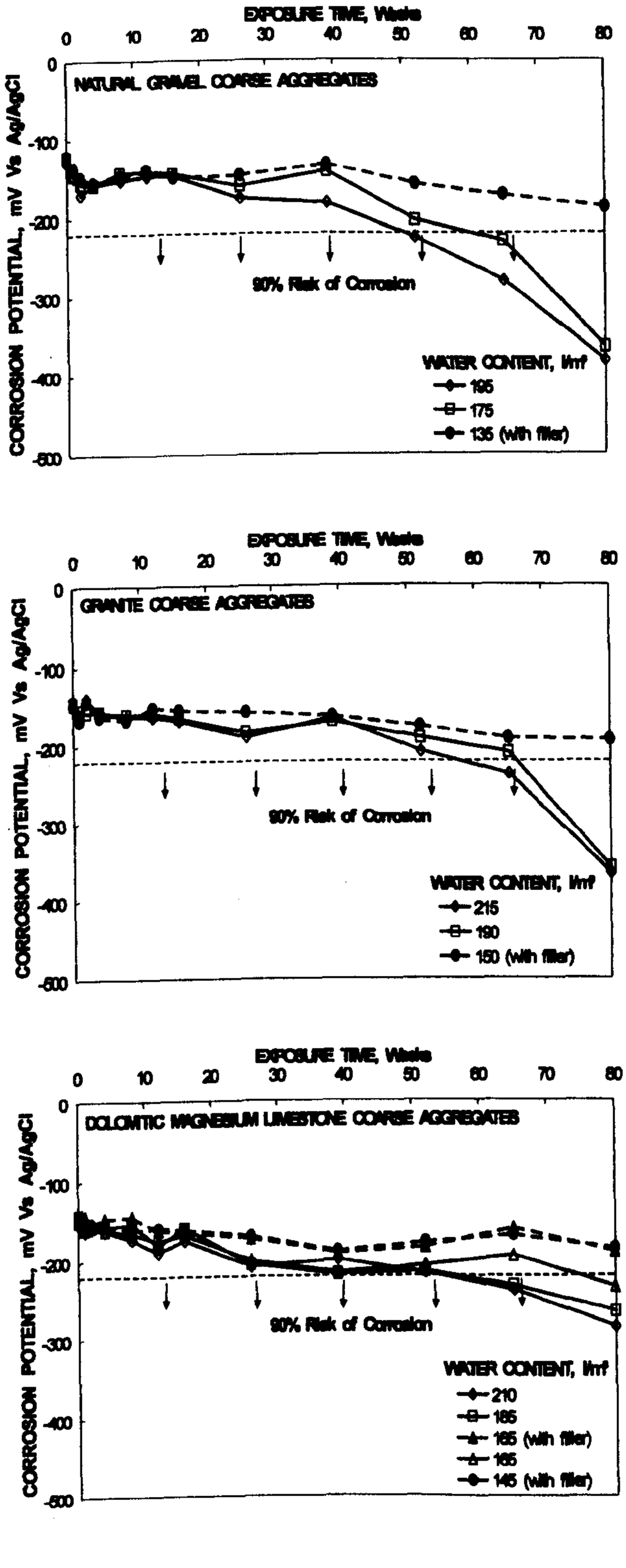
- When corresponding mixes were compared, both PC / PFA and PC / GGBS concrete showed better resistance to chloride penetration compared to PC concrete and PC / GGBS concrete showed the best performance.

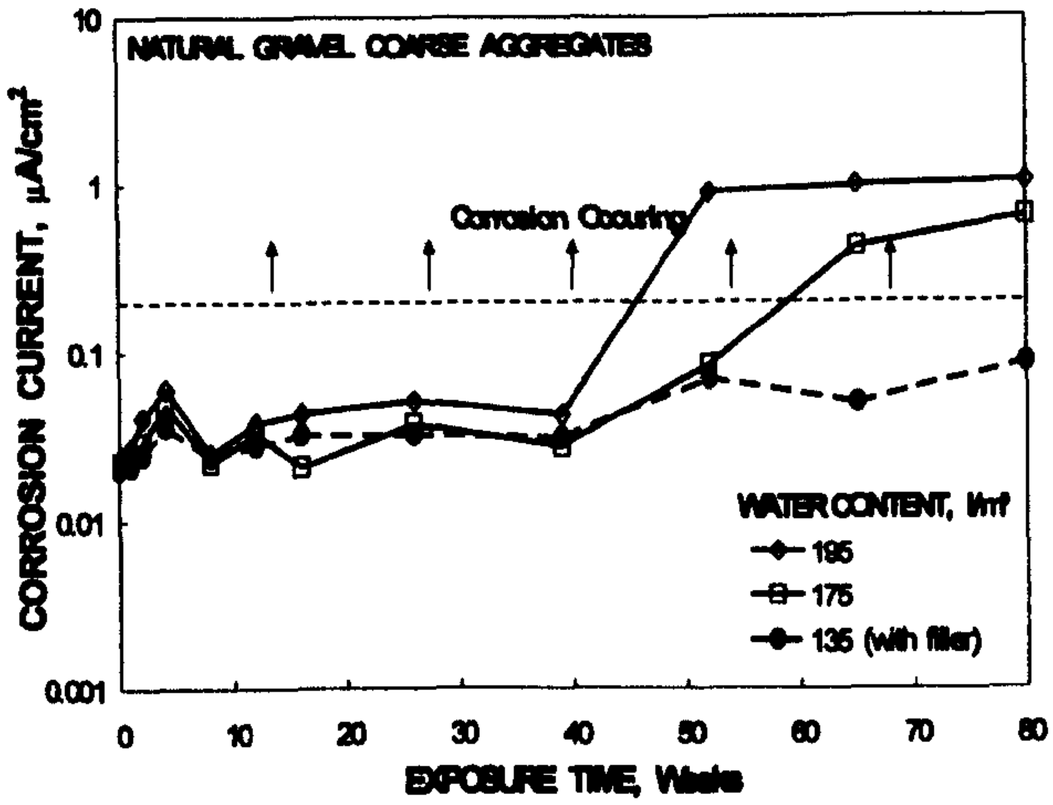
Again, the issues reviewed for chloride diffusion, *i.e.* change in porosity of concrete, tortuosity of flow paths, chloride binding capacity, fines content, ITZ area and improved quality of the cement paste with the use of limestone filler, are applicable in relation to chloride contents with variation in cement and water contents in equal proportion. In addition, it is worth noting that the improved resistance to chloride penetration of both PC / PFA and PC / GGBS concrete and, in particular, better performance of PC / GGBS concrete agree with previous research work (Mangat and Molloy, 1991; McCarthy *et al*, 2001). These relate to the physical and chemical contributions of these cements to improve the microstructure and chloride binding capacity of concrete.

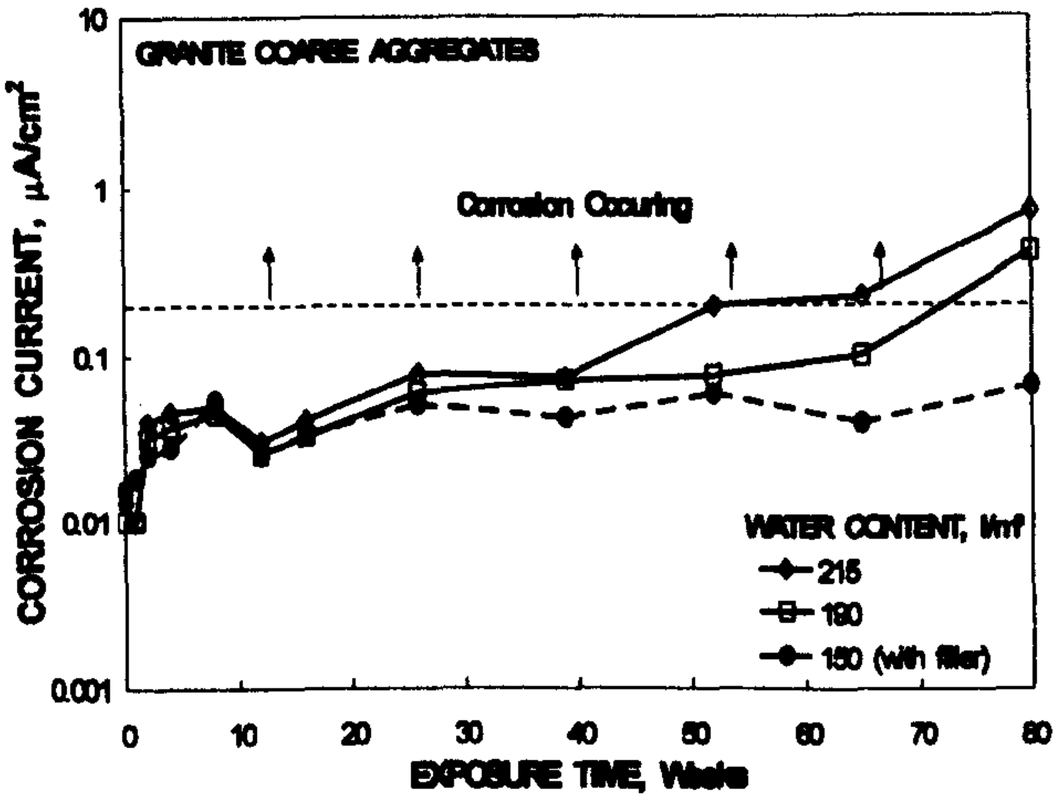
6.2.3 Chloride-Induced Corrosion

Figures 6.3 (a) and (b) show the corrosion potential and current measurements (up to 80 weeks) against the exposure period (6 hours wet (2 M NaCl solution at 20°C) / dry (20°C)) for concrete containing different coarse aggregate and cement types, respectively. The final corrosion potentials, corrosion currents, calculated corrosion rates and rust indices (made by visual inspection of the recovered steel after 80 weeks of exposure) are given in Tables 6.4 (a) and (b) for concrete with different coarse aggregate and cement types, respectively. The classifications used for the visual assessment of recovered steel are given in Table 3.8. The corrosion potentials and currents given in Tables 6.4 (a) and (b), are shown in Figures 6.4 (a) and (b) for concrete made with different coarse aggregate types and in Figures 6.5 (a) and (b) for that made with different cement types, respectively, so that different concrete types can be compared easily.

It should be noted that the corrosion potential and current trends cannot be easily related to the limited data given in the literature, which do not show a clear influence of cement content on the corrosion activities. However, for all concrete types, negative corrosion potentials and currents fluctuated, but increased gradually with exposure period (Figures 6.3 (a) and (b)). It is worth mentioning that similar corrosion behaviour has been observed by previous researchers (Dhir *et al*, 1995; McCarthy *et al*, 2001). In addition, the results followed the trends for chloride build-up (see Figures 6.2 (a) and (b)).







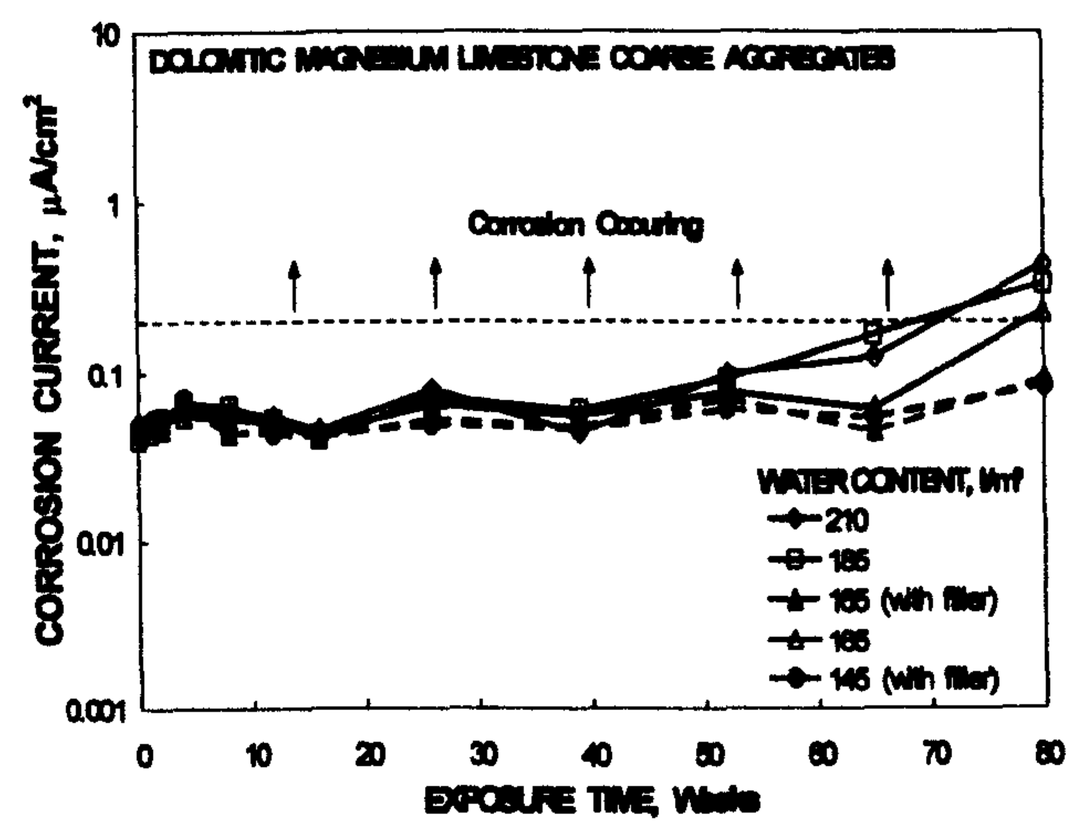


Figure 6.3 (a) Resistance to chloride-induced reinforcement corrosion of concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.45

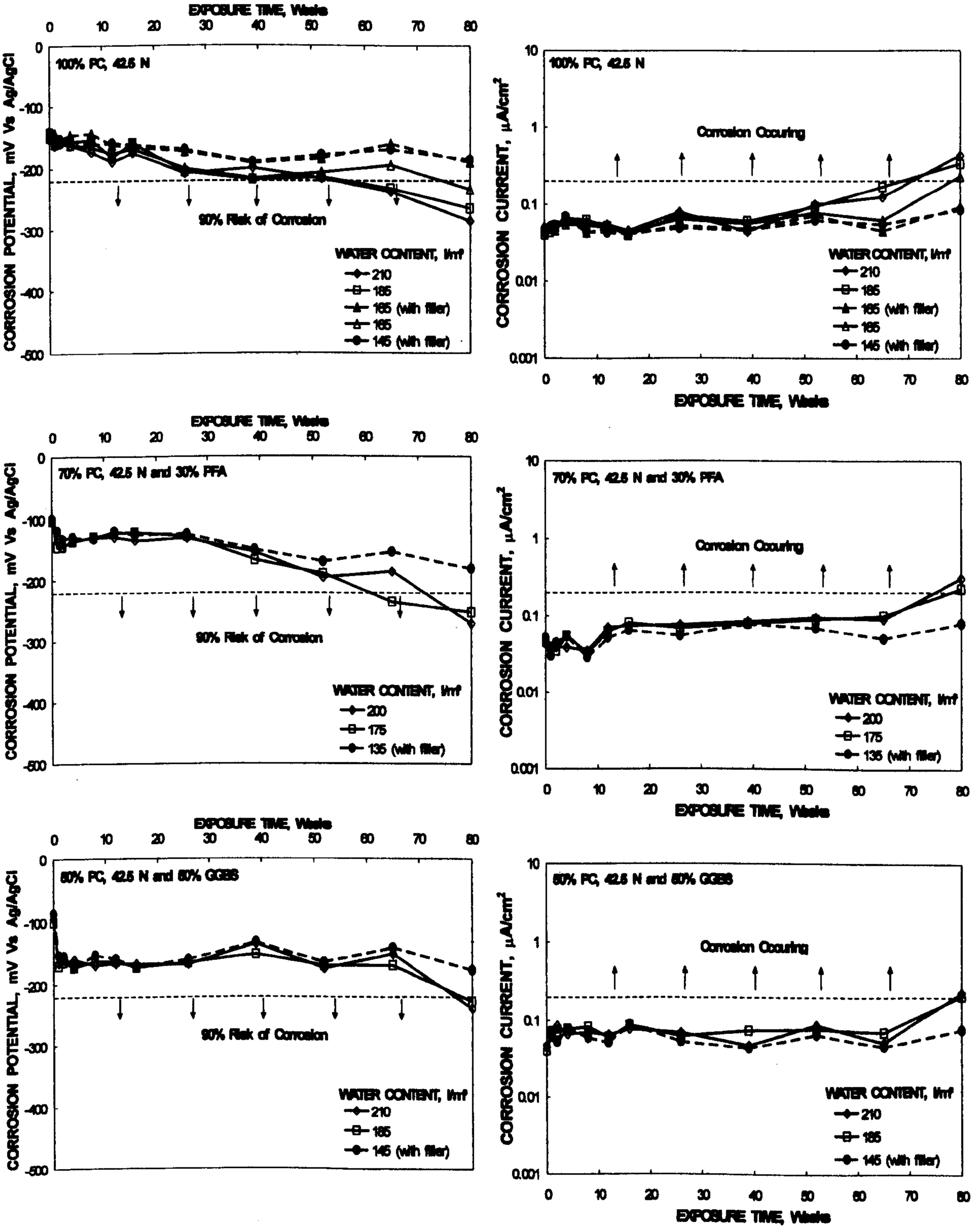


Figure 6.3 (b) Resistance to chloride-induced reinforcement corrosion of concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.45

Table 6.4 Resistance to chloride-induced reinforcement corrosion of concrete

(a) Made with different coarse aggregate types

W/C RATIO	COARSE AGGREGATE	MIX	CORROSION DATA[$] (80 WEEKS)			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.45	Natural Gravel	M5*	-382	1.030	11.9	1 to 2
		M1	-365	0.632	7.3	1 to 2
		M3*f*[#]	-188	0.086	1.0	1
	Granite	M5*	-366	0.709	8.2	1 to 2
		M1	-358	0.406	4.7	1 to 2
		M3*f*[#]	-194	0.066	0.8	1
	Limestone	M5*	-285	0.427	5.0	1 to 2
		M1	-265	0.328	3.8	1
		M2*f*[#]	-190	0.092	1.1	1
		M2[#]	-234	0.225	2.6	1
		M3*f*[#]	-186	0.084	1.0	1

(b) Made with different cement types

W/C RATIO	CEMENT	MIX	CORROSION DATA[$] (80 WEEKS)			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.45	PC, 42.5 N	M5*	-285	0.427	5.0	1 to 2
		M1	-265	0.328	3.8	1
		M2*f*[#]	-190	0.092	1.1	1
		M2[#]	-234	0.225	2.6	1
		M3*f*[#]	-186	0.084	1.0	1
	PC / PFA	M5*	-270	0.300	3.5	1
		M1	-252	0.222	2.6	1
		M3*f*[#]	-181	0.080	0.9	1
	PC / GGBS	M5*	-238	0.228	2.6	1
		M1	-227	0.207	2.4	1
		M3*f*[#]	-177	0.076	0.9	1

[$] 6 hours wet (2 M NaCl solution at 20°C) / dry (20°C) exposure
All mixes in Table (a) contain PC, 42.5 N and natural sand
All mixes in Table (b) contain dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Rust index
1: very slight or no corrosion
2: average corrosion
3: moderate corrosion
4: relatively heavy corrosion

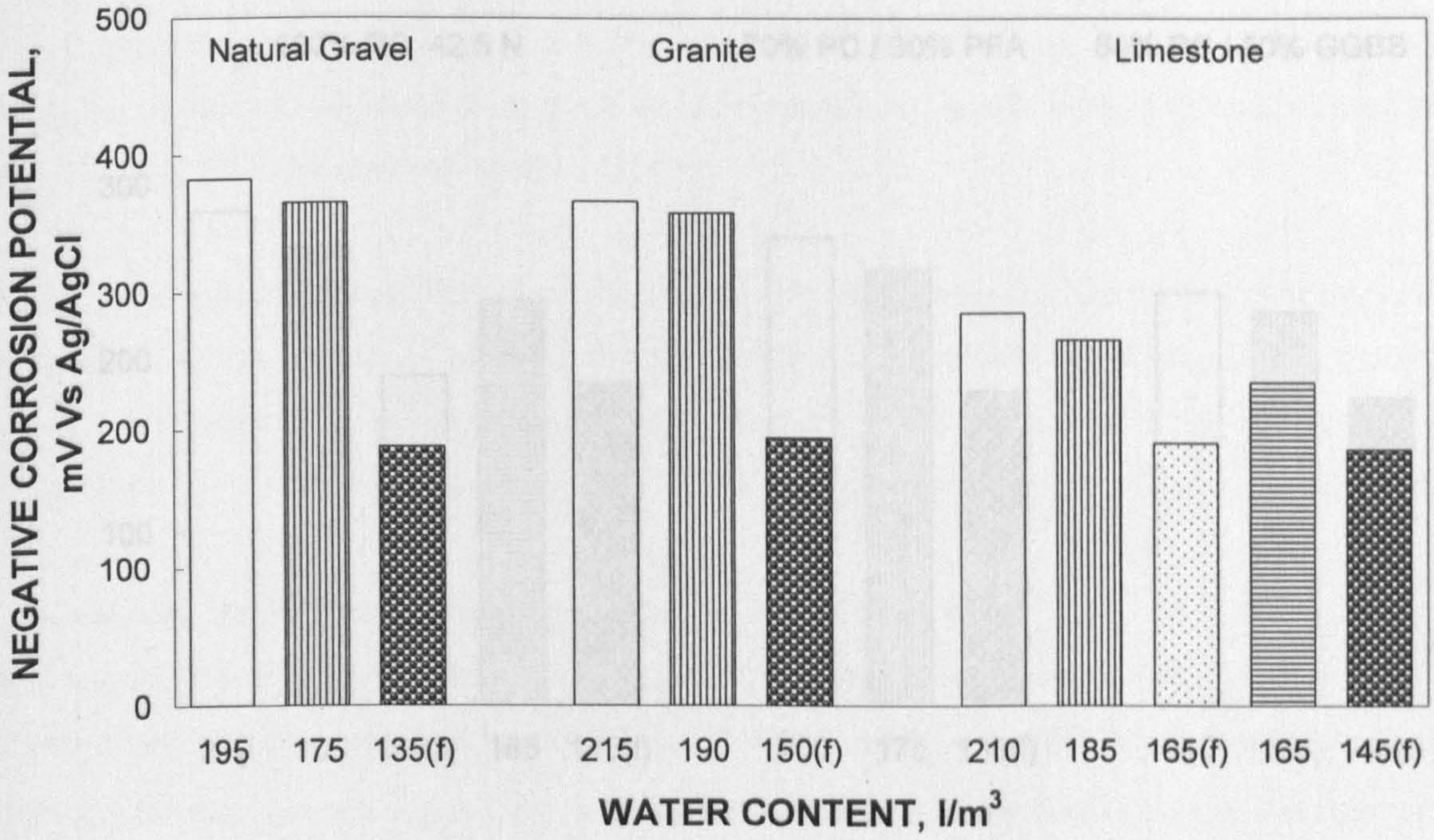


Figure 6.4 (a) Corrosion potentials (80 weeks) of steel in concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.45

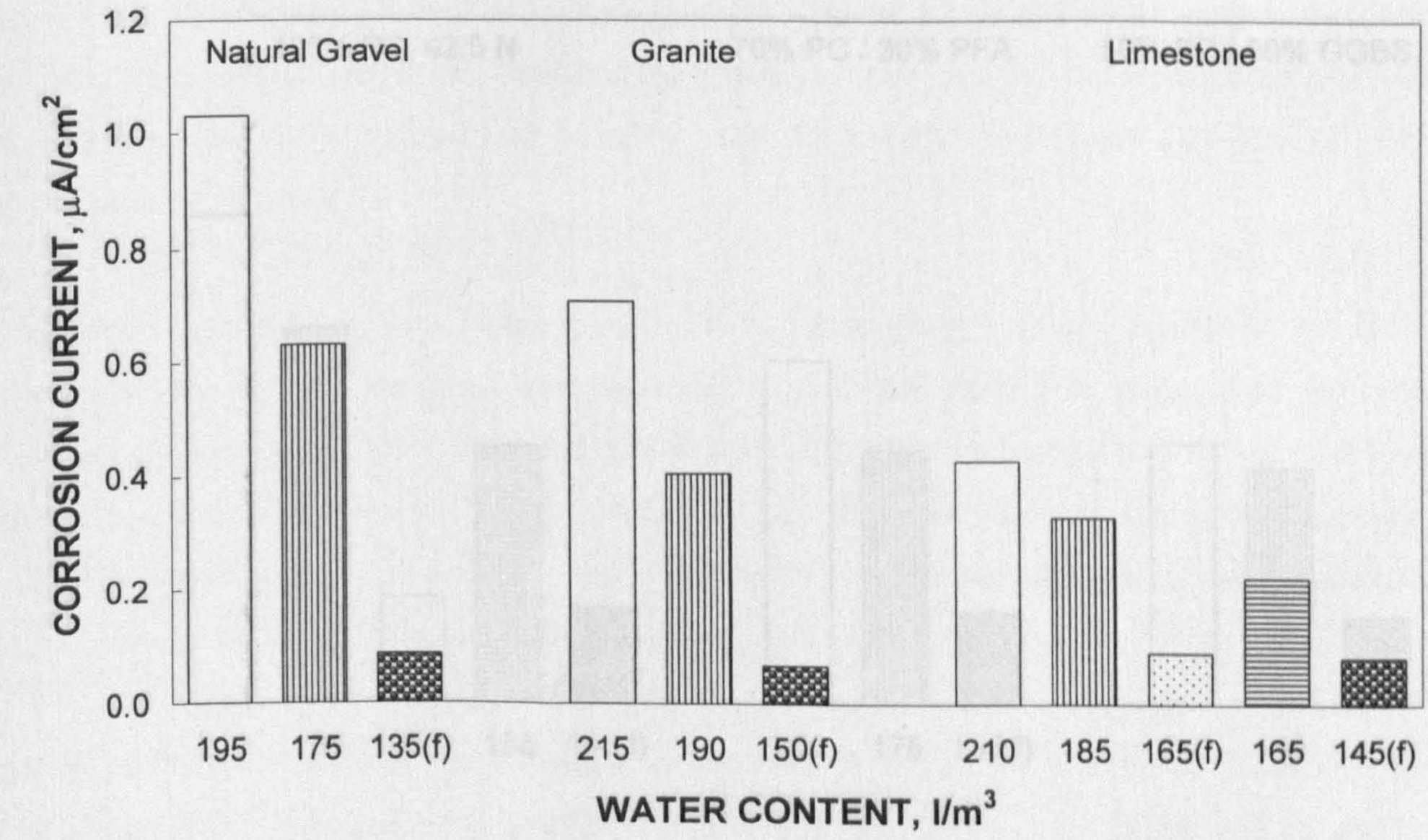


Figure 6.4 (b) Corrosion currents (80 weeks) of steel in concrete made with PC, 42.5 N and different coarse aggregate types, w/c ratio = 0.45

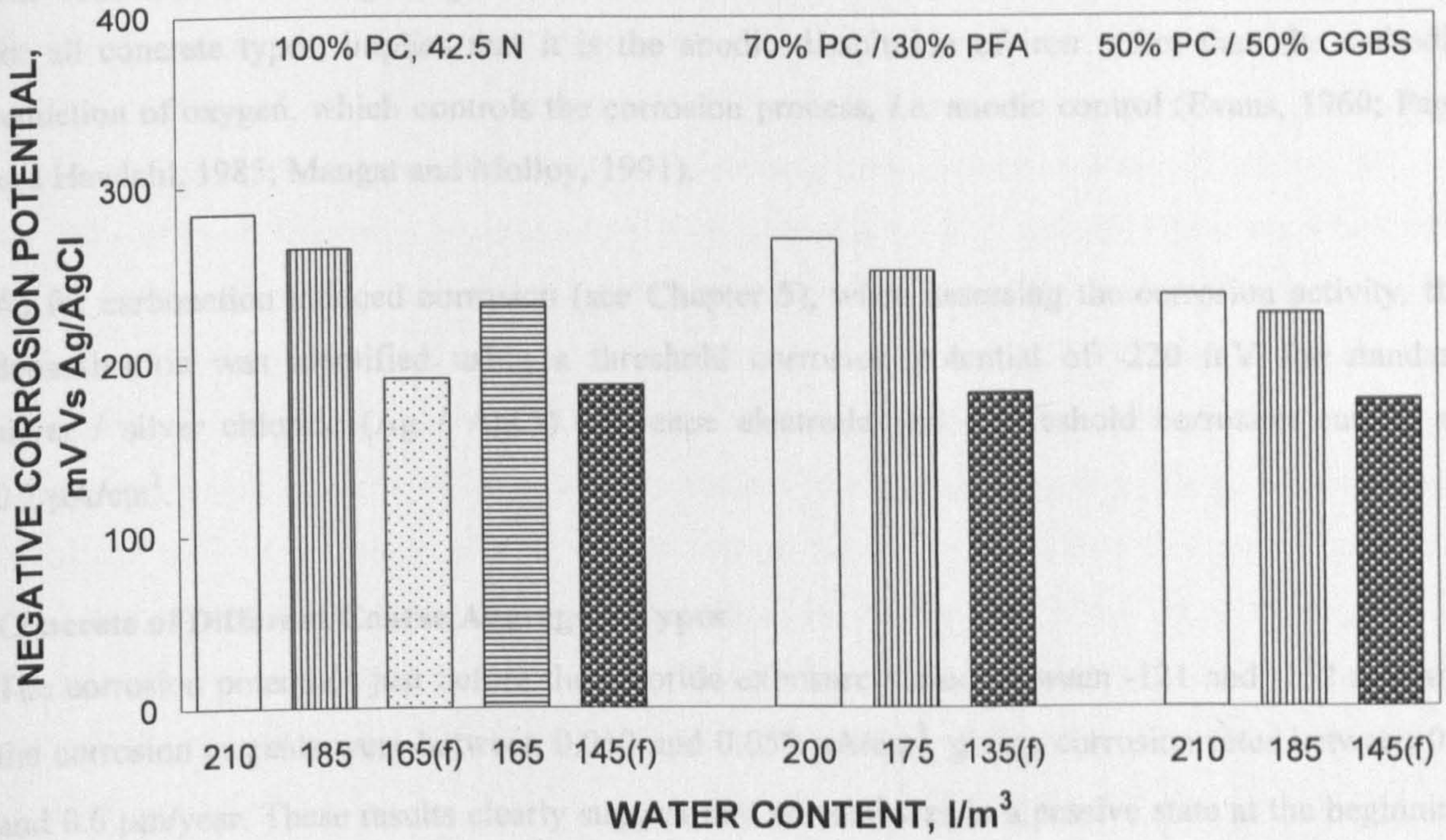


Figure 6.5 (a) Corrosion potentials (80 weeks) of steel in concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.45

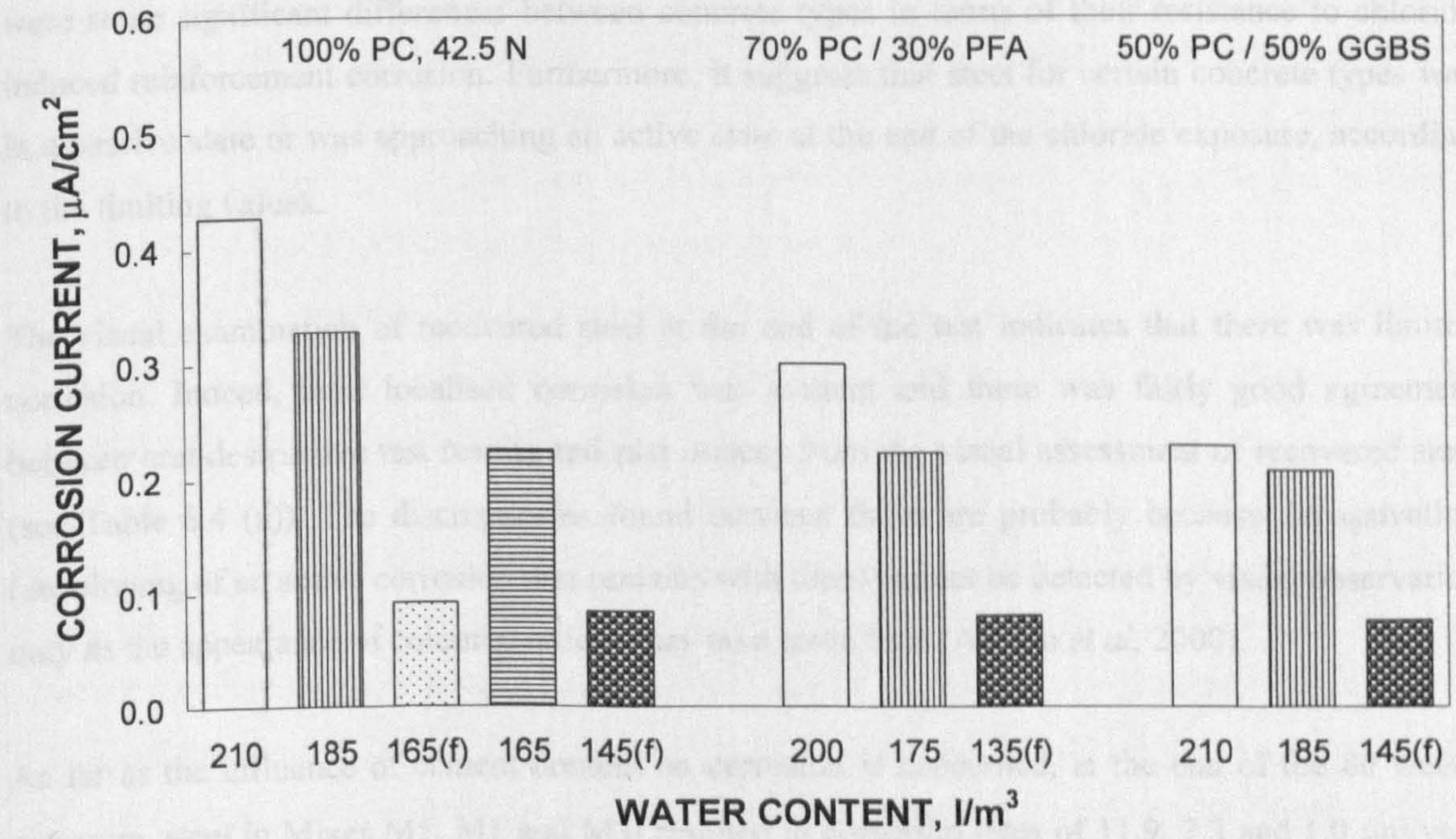


Figure 6.5 (b) Corrosion currents (80 weeks) of steel in concrete made with dolomitic magnesium limestone and different cement types, w/c ratio = 0.45

The behaviour in showing a regular increase in corrosion currents as corrosion potentials decrease for all concrete types, implies that it is the anodic dissolution of iron rather than the cathodic reduction of oxygen, which controls the corrosion process, *i.e.* anodic control (Evans, 1960; Page and Havdahl, 1985; Mangat and Molloy, 1991).

As for carbonation induced corrosion (see Chapter 5), when assessing the corrosion activity, the depassivation was identified using a threshold corrosion potential of -220 mV for standard silver / silver chloride (Ag / AgCl) reference electrode and a threshold corrosion current of 0.2 $\mu A/cm^2$.

Concrete of Different Coarse Aggregate Types

The corrosion potentials just before the chloride exposure varied between -121 and -152 mV and the corrosion currents were between 0.010 and 0.050 $\mu A/cm^2$, giving corrosion rates between 0.1 and 0.6 μm/year. These results clearly suggest that all steel was in a passive state at the beginning of the accelerated exposure, according to the limiting values given above. Thereafter, negative corrosion potentials and corrosion currents increased gradually with exposure period, as mentioned earlier. The corrosion potentials at the end of the 80 weeks exposure period were between -186 and -382 mV. The corrosion currents varied between 0.066 and 1.030 $\mu A/cm^2$ and the corresponding corrosion rates were between 0.8 and 11.9 μm/year (see Table 6.4 (a)). These indicate that there were some significant differences between concrete types in terms of their resistance to chloride induced reinforcement corrosion. Furthermore, it suggests that steel for certain concrete types was in a passive state or was approaching an active state at the end of the chloride exposure, according to the limiting values.

The visual examination of recovered steel at the end of the test indicates that there was limited corrosion. Indeed, light localised corrosion was evident and there was fairly good agreement between non-destructive test results and rust indices from the visual assessment of recovered steel (see Table 6.4 (a)). The discrepancies found between these are probably because depassivation (developing of an active corrosion that remains with time) cannot be detected by visual observation only as the appearance of coloured oxides may take some time (Alonso *et al*, 2000).

As far as the influence of cement content on corrosion is concerned, at the end of the 80 weeks exposure, steel in Mixes M5, M1 and M3*f* resulted in corrosion rates of 11.9, 7.3 and 1.0 μm/year and 8.2, 4.7 and 0.8 μm/year for concrete made with natural gravel and granite, respectively. The corrosion rates of steel in Mixes M5, M1, M2*f*, M2 and M3*f* of concrete made with dolomitic magnesium limestone were 5.0, 3.8, 1.1, 2.6 and 1.0 μm/year, respectively, (see Table 6.4 (a) for

all the corrosion activities at the end of the exposure period, which are of similar order to those observed by previous researchers (Mangat and Molloy, 1991; Mangat and Molloy, 1992; Dhir *et al*, 1995; McCarthy *et al*, 2001)). These results indicate that for concrete made with a particular aggregate type, there were no significant differences in performance between Mixes M5, M1 and M2 (Mix M2 only for concrete made with dolomitic magnesium limestone). However, considering the final corrosion values, these mixes can be ranked as M2, M1 and M5 from highest to the lowest resistance to chloride-induced reinforcement corrosion. However, the differences between them are small and can be ignored for practical purposes. In addition, for concrete with all aggregate types, cement and water contents reduced and limestone filler included (to maintain the fines content equal to that of the Reference Mix (M1)) concrete gave significantly higher resistance to corrosion compared to the other mixes considered. According to the limiting values given earlier, steel in these mixes was just approaching an active state at the end of the chloride exposure. In addition, rust indices and trends for chloride build-up generally agreed with corrosion potential and current measurements.

Therefore, overall, it can be concluded that at w/c ratio 0.45;

- For concrete made with dolomitic magnesium limestone, reduction in cement and water contents (M2) and increasing cement and water contents with workability increase from 75 to 180 mm nominal slump (M5), led to a minor improvement and a reduction in the resistance of concrete to chloride-induced reinforcement corrosion, respectively, compared to the Reference Mix (M1). However, these changes are of limited practical significance. When the filler was included to maintain the fines content equal to that of the Reference Mix (M1), with cement and water reduction, corrosion activity was significantly reduced compared to the Reference Mix (M1). Thus, Mix M3*f* gave the best performance.
- The above patterns were not changed by the use of natural gravel or granite coarse aggregates. In addition, there was no influence of aggregate type on the resistance of concrete to chloride-induced reinforcement corrosion.

As the corrosion results are generally in line with trends for chloride build-up, the mechanisms discussed in Sections 6.2.1 and 6.2.2, *i.e.* change in porosity of concrete, tortuosity of flow paths, chloride binding capacity, fines content, ITZ area and improved quality of the cement paste with the use of limestone filler, are likely to control the corrosion initiation of steel in concrete with different cement contents. However, the threshold chloride content may change with concrete mix proportions (Alonso *et al*, 2000) and, therefore, chloride contents are not the sole factor controlling the corrosion process. Indeed, as mentioned in the literature review, the corrosion activity is influenced by a complex interaction of factors relating to both the concrete characteristics and the environment (Arup, 1983; Page *et al*, 1986; Treadaway, 1988), and the individual contribution of

these factors is difficult to determine (Dhir *et al*, 1995). Similarly, the mechanisms associated with reduction in cement and water contents in equal proportion tend to have both positive and negative effects on the corrosion process and their individual contribution is not easy to quantify.

The reduction in cement and water contents in equal proportion reduced the capillary porosity and improved the permeation properties of concrete (see Section 4.4). These effects may have contributed to reduce corrosion activity with cement reduction due to limiting oxygen availability at the cathode. Indeed, Buenfeld and Okundi (1998) showed that oxygen diffusion coefficients (measured without any applied pressure) reduced slightly with cement and water reductions in equal proportion.

In addition, reduction in cement and water contents in equal proportion generally increased the compressive strength (see Table 6.1(a)) and reduced the porosity of concrete (see Section 4.4.1). This may have contributed to reduce the corrosion, in particular mixes containing limestone filler. Indeed, Glass *et al* (1991) suggest that concrete with a higher compressive strength and a lower porosity would be expected to have a higher resistivity, which may give lower corrosion rates. Moreover, Buenfeld and Okundi (1998) concluded that electrical conductivity of concrete reduced slightly with cement and water reductions in equal proportion.

On the other hand, the quality of the protection afforded to the steel surface is likely to be a function of the electrochemical stability of the steel surface in its environment, in combination with a portlandite-rich layer at the steel-matrix interface (Page, 1975). Therefore, reduced alkali content associated with cement and water reduction might be expected to reduce the quality of the protection hence to increase corrosion risk for steel. However, the observed results indicate that this effect is less significant.

Whilst water-soluble chloride contents at the level of steel in cement-and-water-reduced mixes with filler (M2*f* and M3*f*) were reasonably high (although they were still lower than that of the other mixes) at the end of the 80 weeks exposure period (see Table 6.3 (a)), the low corrosion noted for steel in these mixes is, perhaps, surprising. However, this is not questionable since the results may be attributed to increased resistivity with these concrete types due to the improved concrete microstructure and compressive strength, as discussed earlier. Supporting the results, on the other hand, Dhir *et al* (1995) suggest that there is no specific chloride level at which corrosion initiates and there is no clear relationship between the water-soluble chloride content and the corrosion rate. Indeed, Mangat and Molloy (1992) observed fairly similar corrosion rates and corrosion potentials, despite significant variations in acid-soluble chloride ion concentrations and chloride to hydroxyl ion concentration (Cl^-/OH^-) ratios at the level of the steel in concrete made with different cement

contents, at fixed w/c ratio (see Sections 2.4.4 and 2.4.5). Moreover, this may explain why the influence of aggregate type on corrosion was not pronounced, despite showing increased chloride diffusion coefficients with increasing porosity of aggregates for corresponding concrete mixes.

Concrete of Different Cement Types

The variation in corrosion activity was essentially similar to that of concrete made with different coarse aggregate types. The corrosion potentials prior to chloride exposure varied between -87 and -152 mV and the corrosion currents were between 0.040 and 0.052 $\mu A/cm^2$. Thus, the corresponding corrosion rates were between 0.5 and 0.6 μm/year. Therefore, all steel was in a passive state, according to the limiting values given earlier. Thereafter, negative corrosion potentials and corrosion currents increased gradually with exposure period. The corrosion potentials at the end of the exposure period were between –177 and –285 mV. The corrosion currents varied between 0.076 and 0.427 $\mu A/cm^2$ and the corresponding corrosion rates were between 0.9 and 5.0 μm/year, see Table 6.4 (b). Again, this suggests that steel in certain concrete types was in a passive state or on the point of corrosion initiating, while others were in an active state at the end of the chloride exposure, according to the limiting values given earlier. The visual examination of recovered steel at the end of the exposure period indicated that light localised corrosion was evident. Generally, there was a reasonable agreement between non-destructive test results and rust indices made by visual assessment of recovered steel (see Table 6.4 (b)). However, as for concrete made with different coarse aggregate types, there were some discrepancies between them as well.

When the influence of cement content on corrosion is considered, at the end of the 80 weeks chloride exposure, steel in Mixes M5, M1, M2*f*, M2 and M3*f* of concrete made with PC resulted in corrosion rates of 5.0, 3.8, 1.1, 2.6 and 1.0 μm/year, respectively. Steel in Mixes M5, M1 and M3*f* resulted in corrosion rates of 3.5, 2.6 and 0.9 μm/year and 2.6, 2.4 and 0.9 μm/year for concrete made with PC / PFA and PC / GGBS, respectively (see, Table 6.4 (b) for the corrosion results at the end of the exposure period). There were minor differences between Mixes M5, M1 and M2 (Mix M2 only for concrete made with PC) and may be ignored for practical purposes. However, considering the final corrosion measurements, it can be seen that the performances of Mixes M2 and M5 were slightly better and worse, respectively, compared to the Reference Mix (M1). Mixes M2*f* (used only for concrete made with PC) and M3*f* showed significantly higher resistance to corrosion compared to the other mixes. According to the limiting values given earlier, steel in these mixes was just approaching corrosion initiation at the end of the chloride exposure. In addition, rust indices and trends for chloride build-up were generally in line with corrosion potential and current measurements.

Therefore, it can be concluded that the influence of variation in cement and water contents in equal proportion on resistance of concrete to chloride-induced reinforcement corrosion was not different with the use of PFA or GGBS with PC. However, it is worth noting the following points observed at w/c ratio 0.45;

- The use of PFA or GGBS with PC improved the performance of relevant mixes compared to PC concrete with PC / GGBS concrete giving the best performance.

The mechanisms discussed for concrete made with different coarse aggregate types, as influencing corrosion with variation in cement and water contents in equal proportion, are also applicable to concrete made with different cement types. Thus, improved permeation properties, reduced porosity (see Section 4.4) and increased compressive strength (see Table 6.1(b)) with cement reduction may have limited the oxygen availability at the cathode and increased the resistivity of the concrete, thereby reducing corrosion. On the other hand, the reduced protection afforded to the steel surface due to reduced alkali content with cement reduction may not have been significant in controlling the corrosion risk. In addition, the reduced corrosion activity of steel in cement-and-water-reduced mixes with filler, despite reasonably high water-soluble chloride contents at the level of the steel (although they were still lower than that of the other mixes) at the end of the 80 weeks exposure period (see Table 6.3 (b)), may be due to the increased resistivity with these concretes (due to improved microstructure and compressive strength). Moreover, possible discrepancies between the chloride content and the corrosion rate may also explain the above changes.

Previous research, which suggest that the use of PFA (Rasheeduzzafar *et al*, 1987; Hussain and Rasheeduzzafar, 1994; Dhir *et al*, 1995; Thomas; 1996) or GGBS (Hope and Lp, 1987; Mangat and Molloy, 1991) with PC, improves the resistance of concrete to chloride-induced reinforcement corrosion compared to PC concrete, are in line with the observed results. In addition, the better performance of PC / GGBS concrete has also been reported (McCarthy *et al*, 2001). This is likely to be attributed to the physical and chemical contributions of these cements to improve the microstructure (despite reduced alkalinity due to pozzolanic reactions) and, consequently, to limit the oxygen availability at the cathode and increase the resistivity of the concrete (Hope and Lp, 1987; Rasheeduzzafar *et al*, 1987; Hussain and Rasheeduzzafar, 1994; Dhir *et al*, 1995).

6.3 CONCLUSIONS

The conclusions given below can be drawn from the results in this chapter. Unless otherwise stated, they are based on concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate, *i.e.* the combination of the main cement and aggregate type used for this study. It is worth mentioning again that these conclusions are for water-cured concrete specimens (at 20°C for

28 days) exposed to 5 M NaCl solution at 20°C and 2 M NaCl solution at 20°C (6 hours wet / dry exposure) for chloride diffusion and corrosion tests, respectively. Note that there is a discussion of the practical implications of the findings from this work in Chapter 8.

6.3.1 Chloride Diffusion

- Reduction in cement and water contents in equal proportion led to a minor reduction in chloride diffusion coefficient compared to the Reference Mix. This effect was greatest and most significant when the filler was included to maintain the fines content equal to that of the Reference Mix. Increasing cement and water contents in equal proportion with workability increase, increased the chloride diffusion coefficient slightly compared to the Reference Mix.

- The above observations were not changed by the use of natural gravel or granite coarse aggregates. However, for corresponding mixes, the chloride diffusion coefficient increased with increasing water absorption (thus, porosity) of aggregates. Thus, concrete made with granite resulted in the highest resistance to chloride diffusion and that made with dolomitic magnesium limestone the lowest.

- Again, the observations pointed out above were not influenced by the cement type used. In addition, both PC / PFA and PC / GGBS concrete showed lower chloride diffusion coefficients compared to PC concrete and PC / GGBS concrete resulted in significantly lower values. Moreover, the effect of cement type on chloride diffusion resistance was more pronounced than that of cement content.

6.3.2 Chloride Content at Cover Depth

- Reduction in cement and water contents in equal proportion without the inclusion of limestone filler resulted in a slightly lower chloride content at the level of the steel at a given time during the exposure compared to the Reference Mix. However, when the filler was included to maintain the fines content equal to that of the Reference Mix, significantly lower chloride contents were reported. Increasing cement and water contents in equal proportion with workability increase, resulted in an insignificant change in chloride content at the level of the steel at a given time during the exposure compared to the Reference Mix.

- The above observations were not changed for concrete made with natural gravel or granite coarse aggregates. In addition, when relevant mixes were compared, concrete made with granite coarse aggregates (lowest water absorption) showed the highest resistance to chloride penetration. There were no significant differences in chloride contents at the level of the steel

at a given time during the exposure between concrete made with natural gravel and dolomitic magnesium limestone coarse aggregates.

- As expected, the above observations were not influenced by cement type used. Furthermore, when corresponding mixes were compared, both PC / PFA and PC / GGBS concrete showed better resistance to chloride penetration compared to PC concrete with PC / GGBS giving the best performance.

6.3.3 Chloride-Induced Corrosion

- Reduction in cement and water contents in equal proportion without the inclusion of limestone filler and increasing cement and water contents in equal proportion with workability increase, led to a minor improvement and a reduction in the resistance of concrete to chloride-induced reinforcement corrosion, respectively, compared to the Reference Mix. However, these changes were relatively minor. When the filler was included to maintain the fines content equal to that of the Reference Mix, with reduction in cement and water contents in equal proportion, corrosion was significantly reduced in comparison to the Reference Mix.

- The above behaviour was not changed by the use of natural gravel or granite coarse aggregates. In addition, there was no influence of aggregate type on the resistance of concrete to chloride-induced reinforcement corrosion.

- The above observations were not influenced by the cement type, but the use of PFA or GGBS with PC improved the performance of relevant mixes, compared to PC concrete, with concrete made with PC / GGBS giving the best performance.

CHAPTER 7

ROLE OF CEMENT CONTENT ON RESISTANCE OF CRACKED CONCRETE TO CHLORIDE-INDUCED REINFORCEMENT CORROSION

7.1 INTRODUCTION

The work carried out to examine the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the resistance of uncracked concrete to carbonation-and-chloride-induced reinforcement corrosion was discussed in Chapters 5 and 6, respectively. However, concrete in structures is likely to undergo cracking due to physical, chemical, thermal factors and/or loading. These cracks, potentially, may permit greater migration of moisture, oxygen and aggressive agents through the concrete making the steel more susceptible to corrosion (ACI Committee 224R, 1990; Stewart and Rosowsky, 1997). It is, therefore, appropriate in examining the role of cement content on the resistance of concrete to reinforcement corrosion to extend to cover cracked sections in order that their impact on the overall process can be quantified.

Experience suggests that carbonation-induced corrosion generally causes a less serious damage to reinforced concrete structures and threat to structural integrity than chloride-induced corrosion, which tends to be associated with intense localised attack so that bars become deeply pitted (Page and Treadaway, 1982; Page *et al*, 1986; Mehta, 1991; ACI Committee 222R, 1996). Moreover, De Schutter (1999) suggests that the influence of cracks on the chloride penetration is significantly higher than that on carbonation. Furthermore, the results given in Chapters 5 and 6 showed higher fluctuations in corrosion potentials and currents of the steel in the specimens subjected to chloride-induced corrosion than those subjected to carbonation-induced corrosion, indicating the uncertainties of the former.

Given this background, this study examined the effect of variation in cement and water contents in equal proportion on the resistance of cracked (intersecting) concrete to chloride-induced reinforcement corrosion using beam specimens under static loading conditions. The test programme is the first of its kind in terms of a combination of variation in cement content (at fixed w/c ratio) and cracking. The experimental programme of study, which includes details of the concrete mixes, curing and properties tested, was discussed in Chapter 3 (see Stage 3). Due to limited available time, the experimental work was carried out using only concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate (*i.e.* combination of the main cement and coarse aggregate types used for Stage 2). Following the guidelines given in BS 5328: Part 1 (BSI, 1997), BS EN 206-1 (BSI, 2001) and BS 8500: Part 1 (BSI, 2002), w/c ratio 0.45 and

45 mm cover to reinforcement were used. The cement content was varied below and above the minimum cement contents given in these standards. It has been reported that multi-reinforced, multi-cracked specimens tend to result in macrocell corrosion and passive cracks, which can give problems in interpretation (Suzuki *et al*, 1990). Therefore, single-bar, single-cracked specimens were used for this study. Indeed, similar test specimens have been used by previous researchers (Ohno *et al*, 1996; Schiessel and Raupach, 1997; Li, 2000 and 2001). Given the importance of the crack width, three surface crack widths were selected, namely 0.1, 0.3 and 0.5 mm. 0.1 mm is the boundary between microcracking and macrocracking (Neville, 1995; Li, 2000). 0.3 mm is the maximum permissible crack width for reinforced concrete structures in aggressive environments, according to the guidelines given in BS 8110: Part 2 (BSI, 1985). In addition, 0.5 mm surface crack width was selected as a value beyond the allowable limits.

As described in Section 3.6.5, 28-day water-cured (20°C), reinforced concrete beam specimens (after loading to induce cracks) were exposed to alternative 6 hours wetting (with 3.5% sodium chloride (NaCl) solution at 20°C to simulate sea water) and drying (20°C) cycles. Monitoring of corrosion was made using corrosion potential and polarisation resistance measurements immediately prior to, and periodically during the chloride exposure, see Section 3.6.6. Testing was carried out for 10 weeks. After 1, 4 and 10 weeks of exposure, one specimen for each concrete type or crack width (selectively) was drilled (at both cracked and uncracked zones) to find the water-soluble chloride contents at 30 and 45 mm (the level of the steel) depths, see Section 3.6.7. Samples at 30 mm depth were taken to check the accuracy of the chloride content measurements at 45 mm cover depth and, indeed, for a given mix and crack width, after a given exposure time, chloride content at 30 mm depth was higher than that at 45 mm. As the drilling was destructive, reinforcement bars were recovered for visual assessment (Section 3.6.6).

7.2. RESULTS AND DISCUSSION

Specimens cast with the Reference Mix (M1), the cement-and-water-increased mix with 180 mm nominal slump (M5) and the cement-and-water-reduced (a 40 l/m^3 water reduction) mix with limestone filler (M3*f*) to maintain the fines content equal to that of the Reference Mix (M1), were cracked to 0.3 mm intersecting (cracks cross the reinforcement) surface crack width and tested. In addition, to examine the influence of intersecting crack width on chloride-induced reinforcement corrosion, specimens cast with Mix M5 were cracked to two other surface crack widths (0.1 and 0.5 mm) and tested.

7.2.1 Chloride Content

As the drilled, powdered samples were very small, it was decided to determine only water-soluble chloride contents at the 30 mm depth from the exposed face and at the 45 mm cover depth (level of

the steel). This appears to be sufficient as corrosion is influenced by free chloride ions in the pore solution, it is likely that water-soluble chlorides provide a better indication of those chlorides that are available for corrosion.

Figures 7.1 (a) and (b) show the water-soluble chloride content at the 30 mm depth and 45 mm cover depth (level of the steel), respectively, plotted against the exposure period (6 hours wet with 3.5% NaCl solution at 20°C / dry at 20°C) up to 10 weeks for concrete made with different cement (and water) contents and cracked to 0.3 mm intersecting surface crack width. The chloride contents determined from the samples obtained from uncracked concrete zones (averaged values of Mixes M5, M1 and M3*f*) are also shown in these figures. Similarly, Figures 7.2 (a) and (b) show the water-soluble chloride content at the 30 mm depth and 45 mm cover depth (level of the steel), respectively, plotted against the exposure period up to 10 weeks for the concrete Mix M5, cracked to different intersecting surface crack widths. As for the earlier case, the chloride contents determined from the samples obtained from uncracked concrete zones are also shown in these. The data shown in Figures 7.1 (b) and 7.2 (b), *i.e.* the build-up of chlorides at the level of the steel with time, are given in Tables 7.1 and 7.2, respectively.

The build-up of water-soluble chlorides of all the cracked concrete at the 30 mm depth and 45 mm cover depth (level of the steel) during the salt wet / dry exposure, followed the expected behaviour with chloride content increasing with exposure period but at a reducing rate. Indeed, similar chloride developments have been reported in previous studies (De Schutter, 1999; Li, 2000 and 2001).

A recent review carried out by Alonso *et al* (2000) states that water-soluble chloride threshold can vary between 0.14 and 1.15% by weight of cement and, therefore, the observed chloride contents at the level of the steel indicate a potential for corrosion activity during the exposure period, regardless of the cement content and crack width.

The results indicate that at w/c ratio 0.45;

- For cracked (intersecting) concrete (0.3 mm surface crack width) made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate, reduction in cement and water contents with the inclusion of limestone filler (M3*f*) to maintain the fines content equal to that of the Reference Mix (M1) and increasing cement and water contents with workability increase from 75 to 180 mm nominal slump (M5), resulted in a slight increase and decrease in chloride penetration through the cracked zone, respectively, compared to the Reference Mix (M1). The final water-soluble chloride contents at the level of the steel (after 10 weeks exposure) were

29% higher and 37% lower compared to the Reference Mix (M1) for Mix M3*f* and M5, respectively.

- For the concrete Mix M5, chloride penetration through the cracked zone (intersecting) was controlled by the surface crack width to a certain extent. However, it was not directly proportional to this and, therefore, the final water-soluble chloride contents at the level of the steel (after 10 weeks exposure) were 15% lower and 5% higher for concrete cracked to 0.1 and 0.5 mm widths, respectively, compared to that of 0.3 mm surface crack width (the maximum allowable crack width for reinforced concrete structures in aggressive environments, as given in BS 8110: Part 2 (BSI, 1985)). The measured chloride contents determined from samples taken from uncracked sections were significantly lower compared to those obtained from cracked sections, and the final water-soluble chloride content at the level of the steel (after 10 weeks) of uncracked concrete was 85% lower than that of cracked (0.3 mm surface crack width) concrete.

It appears that the mechanisms associated with variation in cement and water contents in equal proportion to control the chloride penetration through uncracked concrete (see Sections 6.2.1 and 6.2.2), are very unlikely to dominate when cracks are present, where the flow mechanism (chloride ingress through cracks directly) is more dominant than the diffusion mechanism. It is worth noting that when the chloride ion content is expressed as a percentage of the weight of cement, cement-reduced mixes are likely to show higher chloride contents due to their low cement contents and this may partly explain the increase in chloride contents with cement and water reduction. In addition, reduction in chloride binding capacity with cement reduction may also have contributed.

Li, (2000 and 2001) suggests that when the crack width is greater than 0.1 mm, the diffusion mechanism becomes much weaker and the flow mechanism becomes dominant. This explains the increase in chloride penetration through concrete with increasing surface crack width from 0.1 to 0.5 mm. Furthermore, Li (2001) states that after the concrete is saturated with chloride ions, the crack width does not make much difference in chloride build-up. Indeed, this fact supports the observed results, as the chloride penetration through concrete was not directly proportional to the surface crack width varying from 0.1 to 0.5 mm.

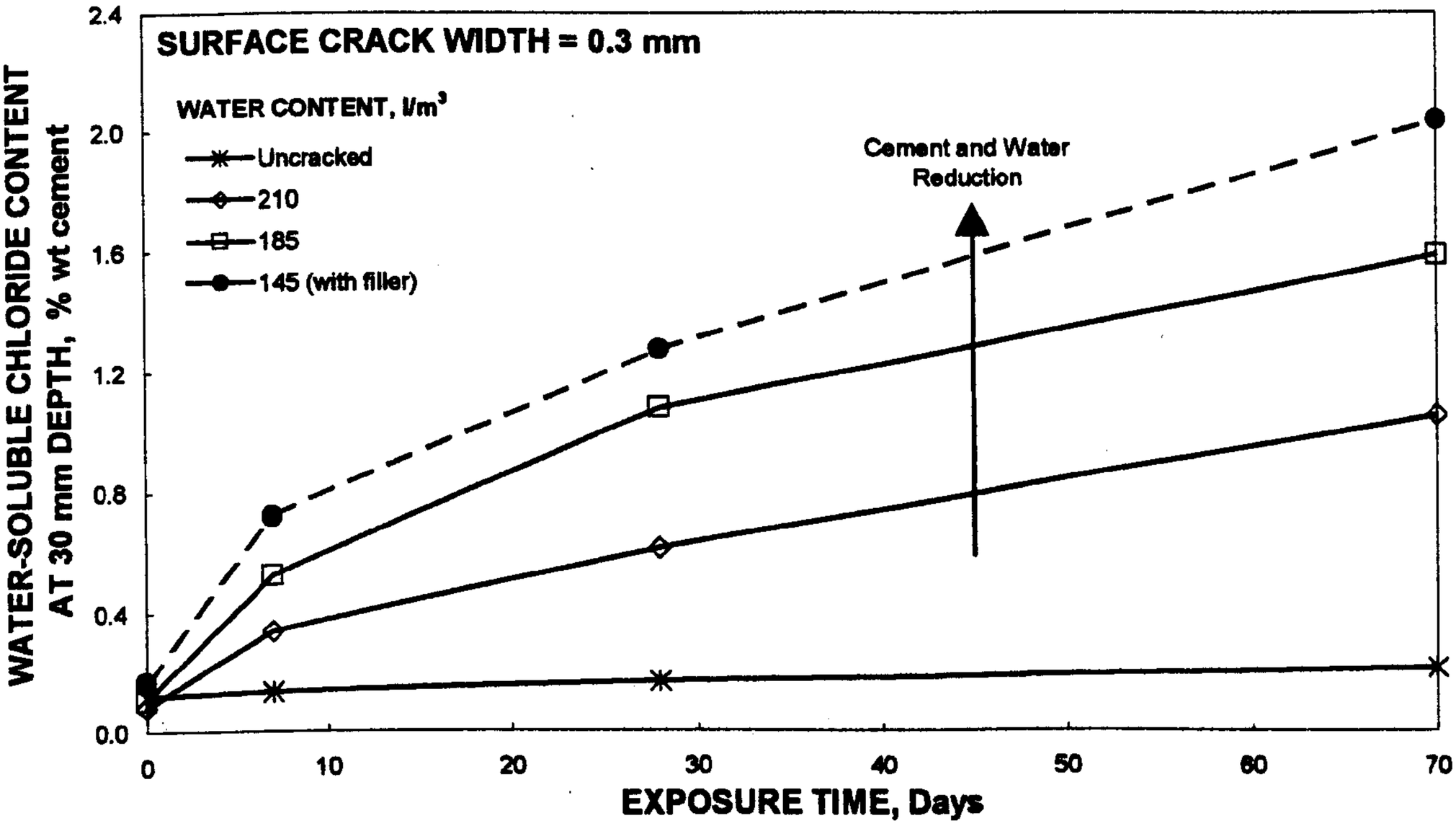


Figure 7.1 (a) Influence of cement content on resistance to chloride penetration to 30 mm depth of cracked (intersecting) concrete, w/c ratio = 0.45

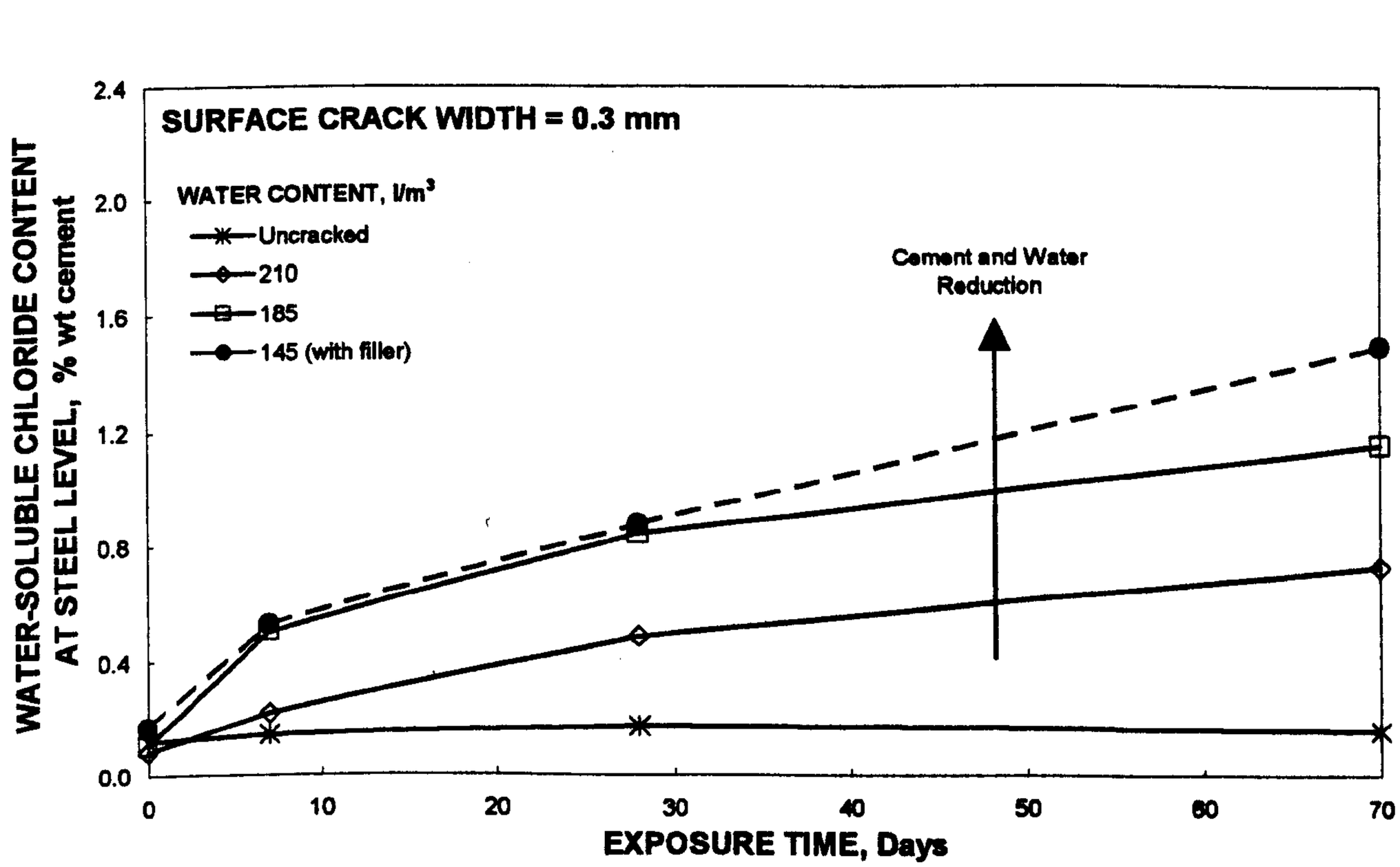


Figure 7.1 (b) Influence of cement content on resistance to chloride penetration to 45 mm depth of cracked (intersecting) concrete, w/c ratio = 0.45

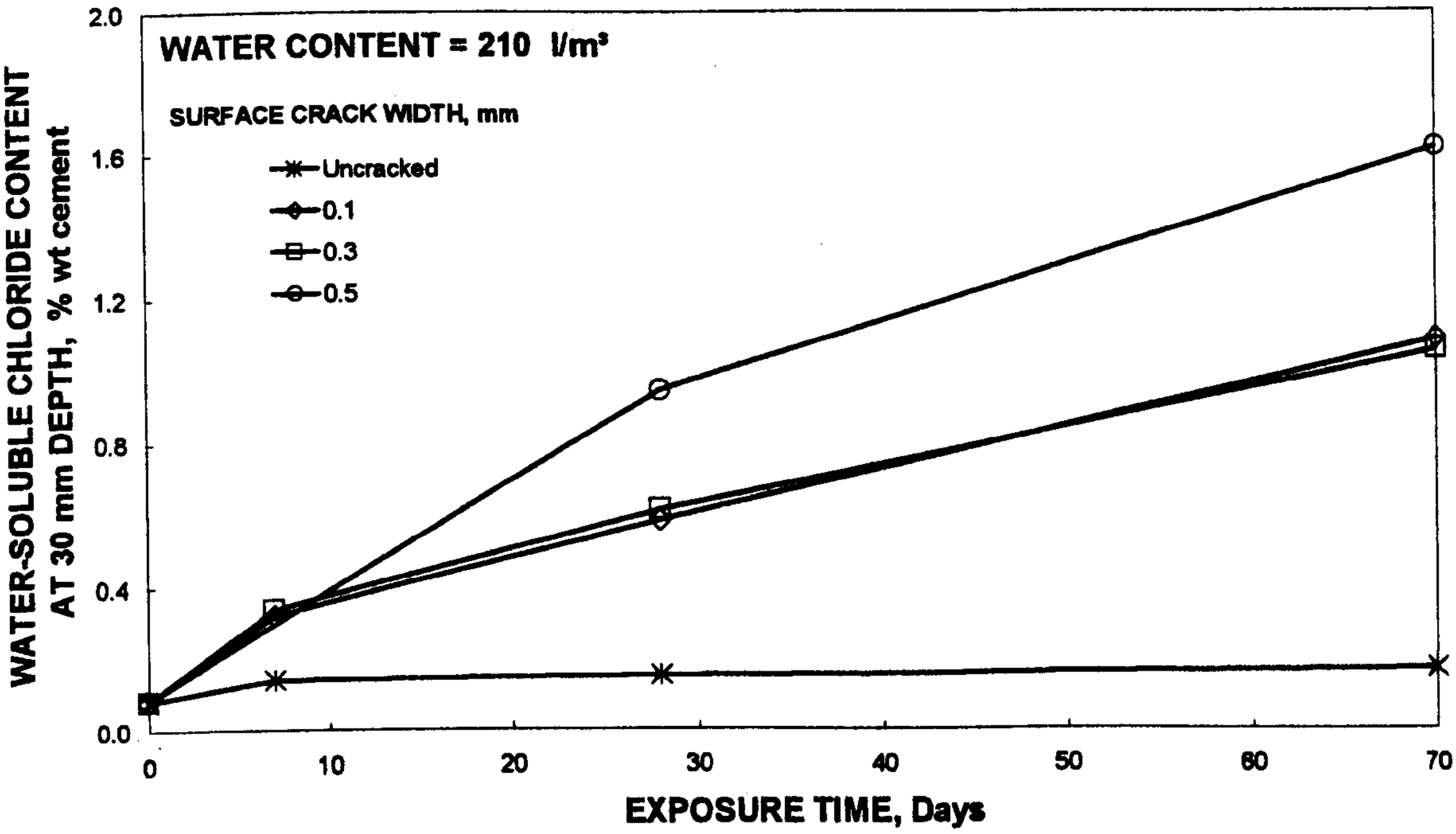


Figure 7.2 (a) Influence of intersecting crack width on resistance to chloride penetration to 30 mm depth of concrete, w/c ratio = 0.45

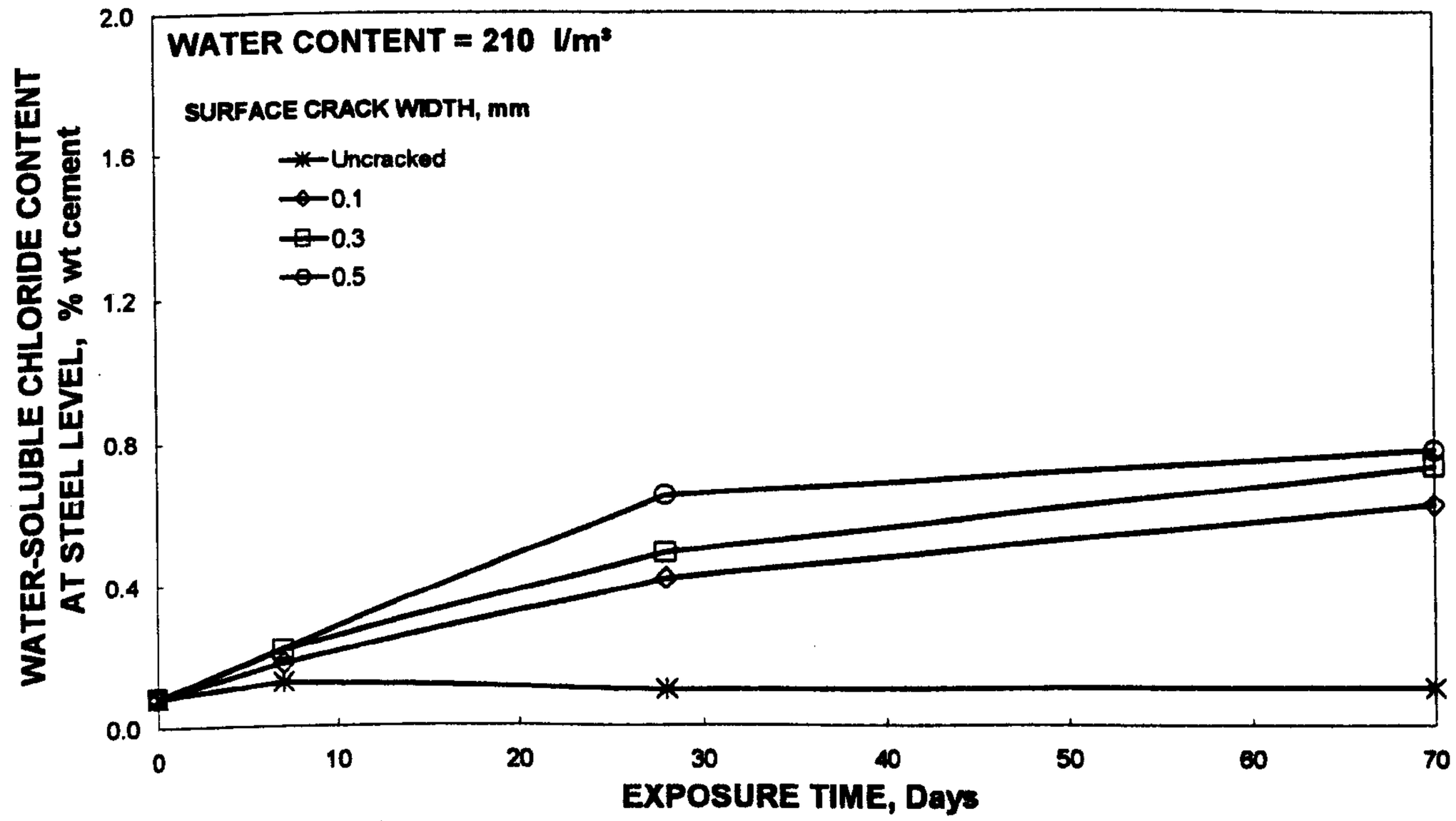


Figure 7.2 (b) Influence of intersecting crack width on resistance to chloride penetration to 45 mm depth of concrete, w/c ratio = 0.45

Table 7.1 Influence of cement content on resistance to chloride penetration of cracked (intersecting) concrete

W/C RATIO	MIX	WATER-SOLUBLE CHLORIDE CONTENT AT STEEL LEVEL[$]							
		% by weight of cement				% of M1			
		0 week	1 week	4 weeks	10 weeks	0 week	1 week	4 weeks	10 weeks
0.45	Uncracked	0.12	0.14	0.17	0.16	---	---	---	---
	M5*	0.08	0.22	0.49	0.73	80	44	58	63
	M1	0.10	0.50	0.84	1.15	100	100	100	100
	M3*f*[#]	0.17	0.53	0.88	1.48	170	106	105	129

[$] 6 hours wet (3.5% NaCl solution at 20°C) / dry (20°C) exposure
Surface crack width is 0.3 mm
All mixes contain PC, 42.5 N, dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1

Table 7.2 Influence of intersecting crack width on resistance to chloride penetration of concrete

W/C RATIO	SURFACE CRACK WIDTH, mm	WATER-SOLUBLE CHLORIDE CONTENT AT STEEL LEVEL[$]							
		% by weight of cement				% of 0.3 mm surface crack width			
		0 week	1 week	4 weeks	10 weeks	0 week	1 week	4 weeks	10 weeks
0.45	Uncracked	0.08	0.13	0.10	0.11	100	59	20	15
	0.1	0.08	0.18	0.41	0.62	100	82	84	85
	0.3	0.08	0.22	0.49	0.73	100	100	100	100
	0.5	0.08	n/t	0.65	0.77	100	n/t	133	105

[$] 6 hours wet (3.5% NaCl solution at 20°C) / dry (20°C) exposure
Concrete contains PC, 42.5 N, dolomitic magnesium limestone and natural sand
Water content is 210 l/m^3
Nominal slump is 180 mm
n/t Not tested

7.2.2 Chloride-Induced Corrosion

Figure 7.3 shows the corrosion potential and current measurements plotted against the exposure period (6 hours wet with 3.5% NaCl solution at 20°C / dry at 20°C) up to 10 weeks for steel in cracked (0.3 mm intersecting surface crack width) concrete made with different cement (and water) contents. Similarly, Figure 7.4 shows the corrosion potentials and currents plotted against the exposure period up to 10 weeks for steel in the concrete Mix M5, cracked to different intersecting surface crack widths. The corrosion potentials, corrosion currents, calculated corrosion rates and rust indices (made by visual inspection of the recovered steel) after 1,4 and 10 weeks of exposure, are given in Tables 7.3 and 7.4 for steel in concrete made with different cement (and water) contents (0.3 mm intersecting surface crack width) and for steel in concrete cracked to different intersecting surface crack widths (Mix M5), respectively. The classifications used for visual

assessment of the recovered steel are given in Table 3.8. The corrosion potentials and currents given in Tables 7.3 and 7.4, are shown in Figures 7.5 (a) and (b) for concrete made with different cement (and water) contents (0.3 mm intersecting surface crack width) and in Figures 7.6 (a) and (b) for concrete cracked to different intersecting surface crack widths (Mix M5), respectively, for easy comparison.

As discussed in Chapters 5 and 6, the depassivation of steel bars embedded in concrete was identified using a threshold corrosion potential of -220 mV for standard silver / silver chloride (Ag / AgCl) reference electrode and a threshold corrosion current of 0.2 $\mu A/cm^2$. In addition, visual observations of recovered steel were used to examine for the presence and level of corrosion (after predetermined time intervals of chloride exposure).

Just prior to the chloride exposure, the corrosion potentials of steel in all concrete types varied between -95 and -159 mV. This suggests that all steel was in a passive state. Thereafter, the negative corrosion potentials fluctuated, but increased gradually with exposure period and reached peak values after about 4 to 6 weeks (Figures 7.3 and 7.4). On reaching the peak values, the corrosion potentials remained approximately constant. It is worth mentioning that for steel in cracked (intersecting) concrete, similar corrosion behaviour has been observed by previous researchers (Ohno *et al*, 1996; Li, 2000 and 2001). In addition, the results generally followed the trends for chloride build-up (see Figures 7.1 and 7.2). The corrosion potentials at the end of the exposure period (10 weeks) were between -219 and -318 mV. This suggests that steel bars were in or approaching an active corrosion state at the end of the chloride exposure, according to the limiting value given above.

It should to be noted that the depassivation was not detectable from the measured corrosion currents, which fluctuated in a near horizontal band (0.030 and 0.122 $\mu A/cm^2$) below the threshold corrosion current of 0.2 $\mu A/cm^2$ (Figures 7.3 and 7.4). This was due to the small anodic (at the base of the crack) to cathodic (exposed area of steel) area ratio. Indeed, Alonso *et al* (2000) mention that if the total anodic to cathodic area ratio is very small, the corrosion current may not increase beyond 0.1 $\mu A/cm^2$. In the current study, the Author was aware that the depassivation area was normally very small and coincident with the crack. However, the location of the crack could not be controlled during loading and, therefore, it was decided to use a longer exposed length (uncoated). However, it was still possible to compare the corrosion currents of steel in the different concrete types.

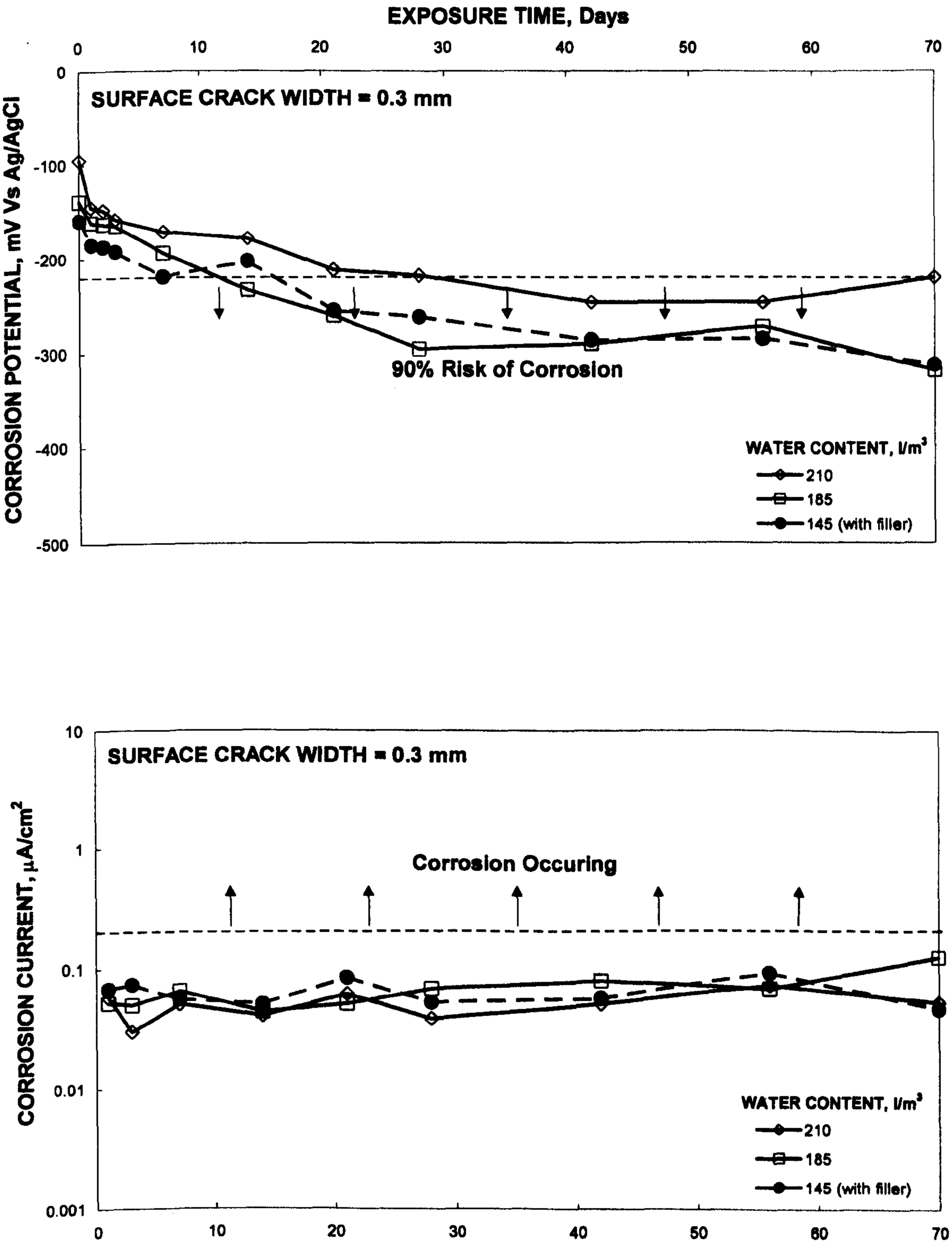


Figure 7.3 Influence of cement content on resistance to chloride-induced reinforcement corrosion of cracked (intersecting) concrete, w/c ratio = 0.45

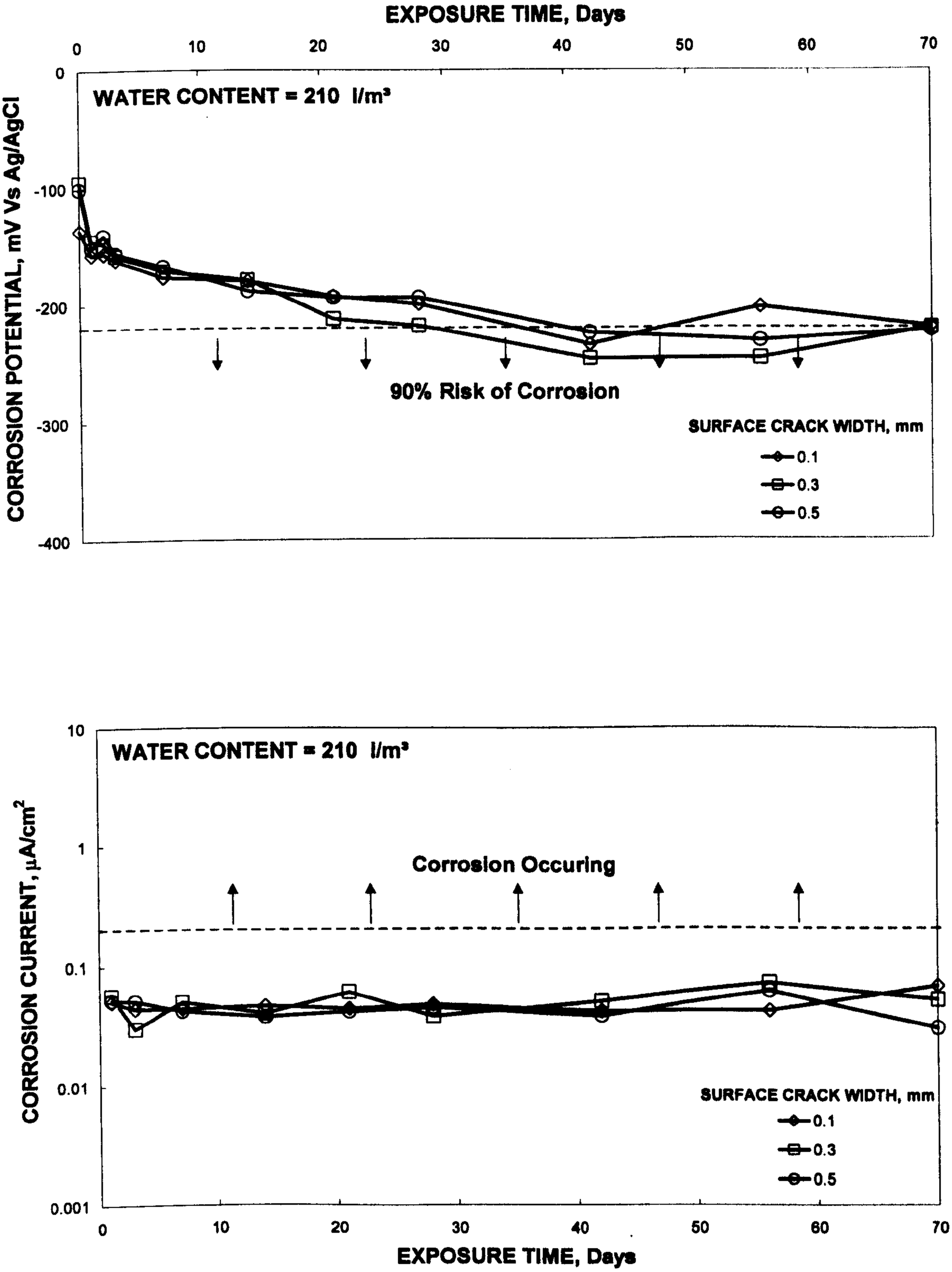


Figure 7.4 Influence of intersecting crack width on resistance to chloride-induced reinforcement corrosion of concrete, w/c ratio = 0.45

Table 7.3 Influence of cement content on resistance to chloride-induced reinforcement corrosion of cracked (intersecting) concrete

W/C RATIO	EXPOSURE TIME, Weeks	MIX	CORROSION DATA[$]			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.45	1	M5*	-171	0.051	0.6	1
		M1	-194	0.065	0.8	1
		M3*f*[#]	-219	0.056	0.6	1
	4	M5*	-218	0.038	0.4	1
		M1	-296	0.067	0.8	1
		M3*f*[#]	-262	0.052	0.6	1
	10	M5*	-220	0.052	0.6	1
		M1	-318	0.122	1.4	1
		M3*f*[#]	-312	0.046	0.5	1

[$] *6 hours wet (3.5% NaCl solution at 20°C) / dry (20°C) exposure*
Surface crack width is 0.3 mm
All mixes contain PC, 42.5 N, dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
[#] *Superplastizer added to maintain workability*
f Filler included to maintain fines content equal to that of M1

Table 7.4 Influence of intersecting crack width on resistance to chloride-induced reinforcement corrosion of concrete

W/C RATIO	EXPOSURE TIME, Weeks	SURFACE CRACK WIDTH, mm	CORROSION DATA[$]			
			Potential, mV	Current, μA/cm²	Rate, μm/yr	Rust Index
0.45	1	0.1	-177	0.045	0.5	1
		0.3	-171	0.051	0.6	1
		0.5	-167	0.043	0.5	n/t
	4	0.1	-200	0.048	0.6	1
		0.3	-218	0.038	0.4	1
		0.5	-194	0.045	0.5	1
	10	0.1	-219	0.067	0.8	1
		0.3	-220	0.052	0.6	1
		0.5	-222	0.030	0.3	1

[$] *6 hours wet (3.5% NaCl solution at 20°C) / dry (20°C) exposure*
Concrete contains PC, 42.5 N, dolomitic magnesium limestone and natural sand
Water content is 210 l/m³
Nominal slump is 180 mm
n/t Not tested

Rust index
1: very slight or no corrosion
2: average corrosion
3: moderate corrosion
4: relatively heavy corrosion

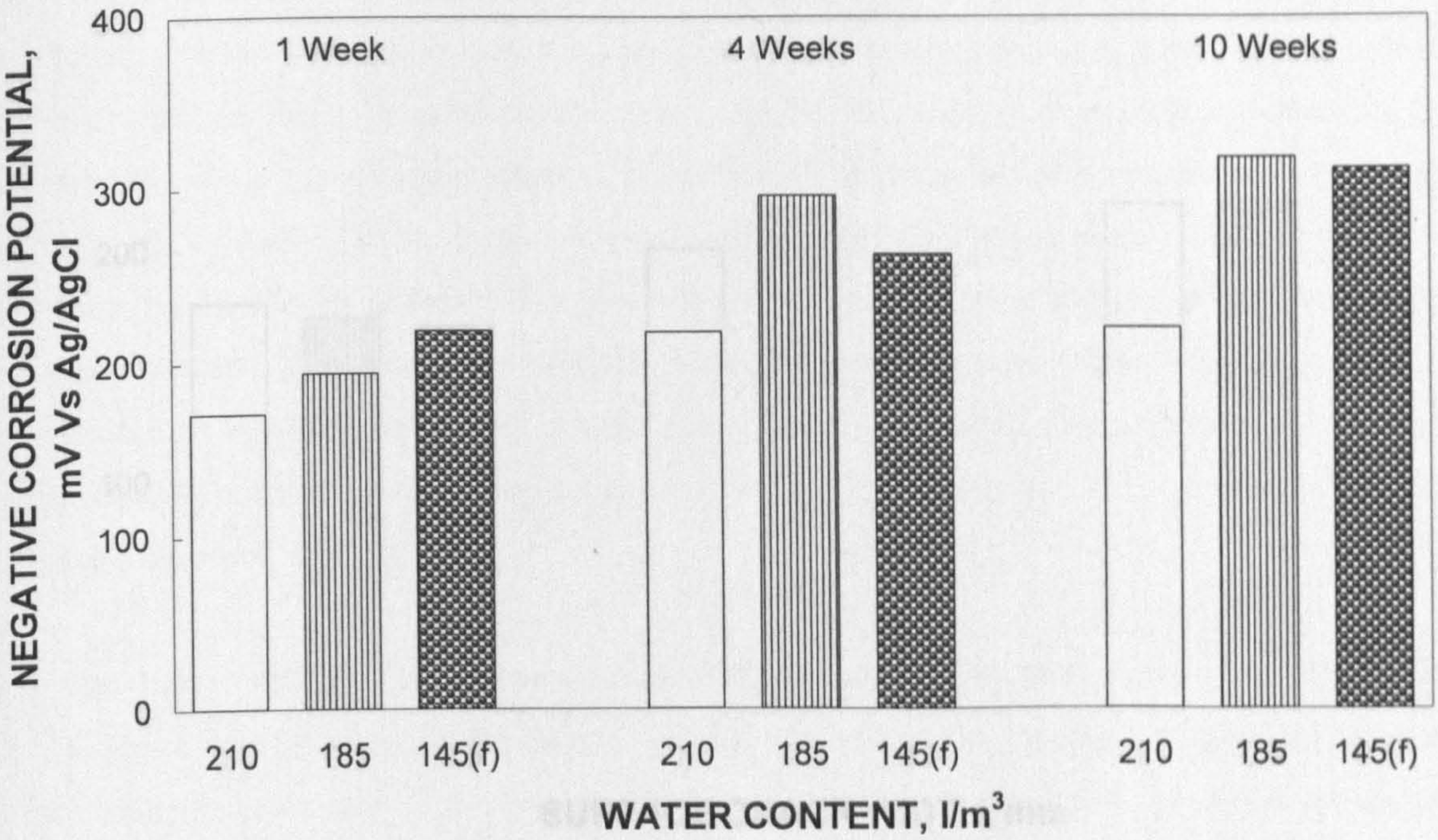


Figure 7.5 (a) Corrosion potentials of steel in cracked concrete (0.3 mm intersecting surface crack width), w/c ratio = 0.45

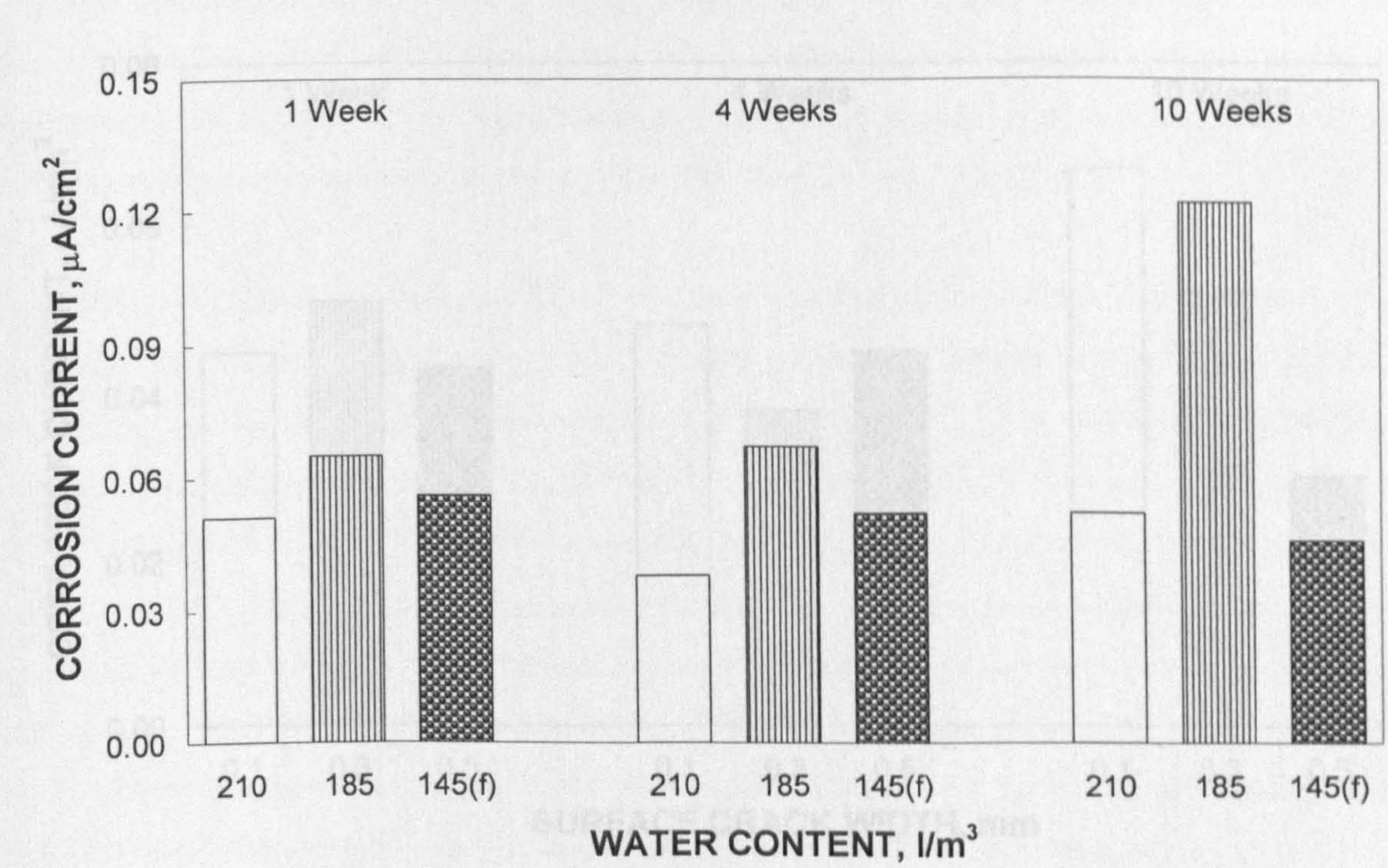


Figure 7.5 (b) Corrosion currents of steel in cracked concrete (0.3 mm intersecting surface crack width), w/c ratio = 0.45

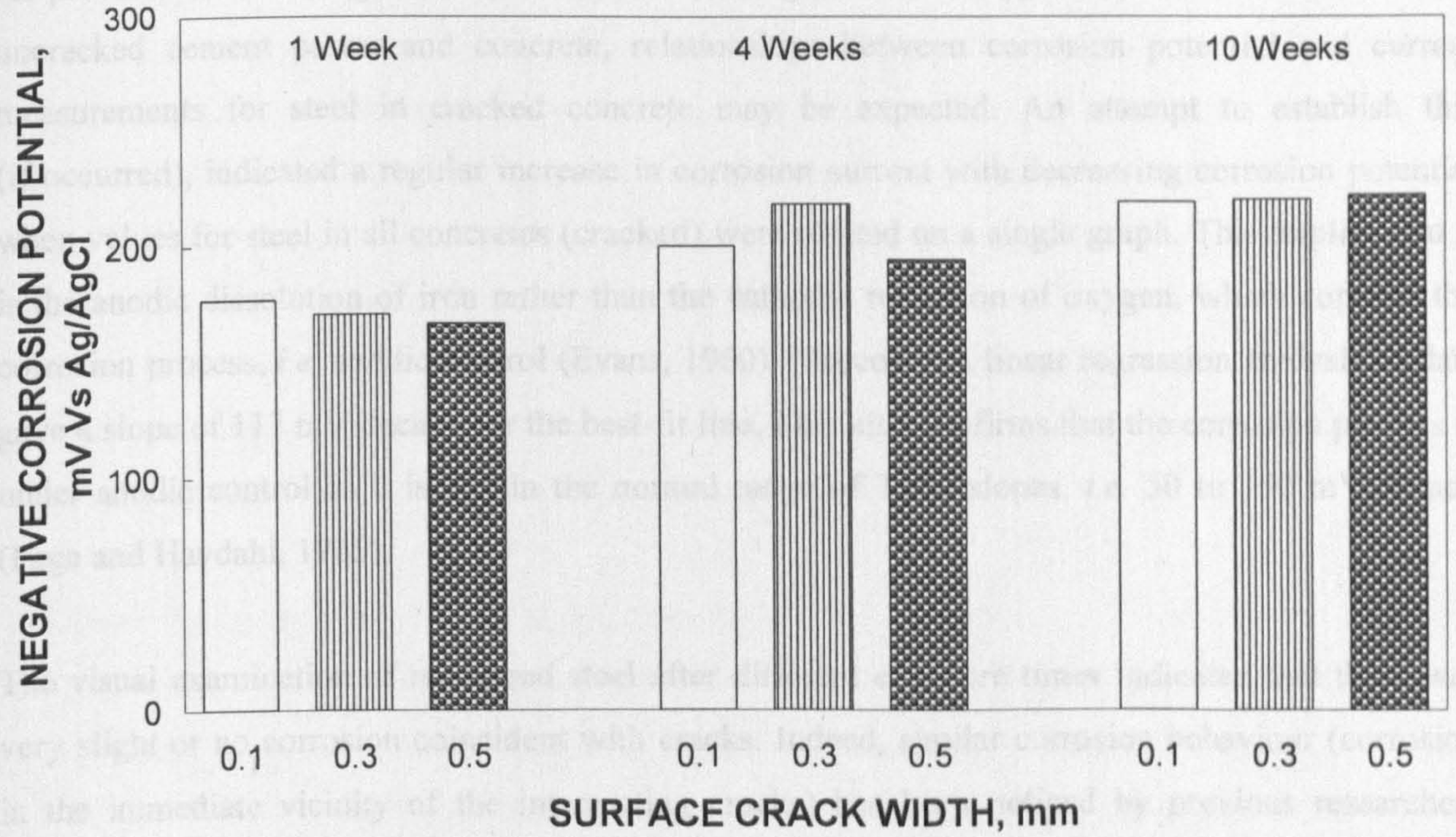


Figure 7.6 (a) Corrosion potentials of steel in cracked (intersecting) concrete (210 l/m^3 water content), w/c ratio = 0.45

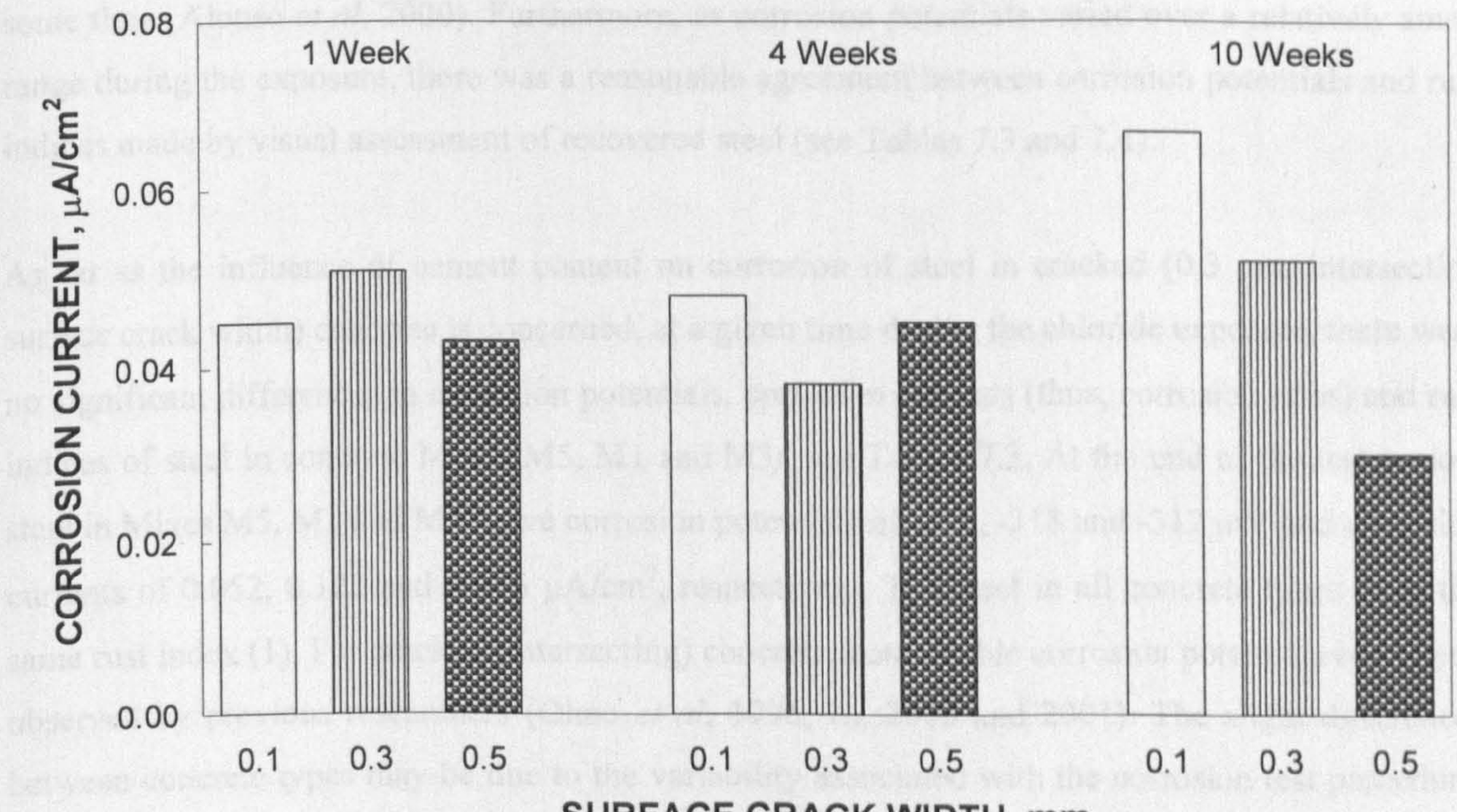


Figure 7.6 (b) Corrosion currents of steel in cracked (intersecting) concrete (210 l/m^3 water content), w/c ratio = 0.45

As previous studies (Page and Havdahl, 1985; Mangat and Molloy, 1991) confirmed for steel in uncracked cement pastes and concrete, relationships between corrosion potential and current measurements for steel in cracked concrete may be expected. An attempt to establish this (if occurred), indicated a regular increase in corrosion current with decreasing corrosion potential when values for steel in all concretes (cracked) were plotted on a single graph. This implies that it is the anodic dissolution of iron rather than the cathodic reduction of oxygen, which controls the corrosion process, *i.e.* anodic control (Evans, 1960). Moreover, a linear regression analysis of data gave a slope of 117 mV/decade for the best-fit line. This also confirms that the corrosion process is under anodic control as it is within the normal range of Tafel slopes, *i.e.* 50 to 150 mV/decade (Page and Havdahl, 1985).

The visual examination of recovered steel after different exposure times indicated that there was very slight or no corrosion coincident with cracks. Indeed, similar corrosion behaviour (corrosion in the immediate vicinity of the intersecting cracks) has been noticed by previous researchers (Ohno *et al*, 1996; Li, 2000 and 2001). Whilst corrosion potential readings generally indicated signs of depassivation after 2 to 4 weeks, the outcome of the visual assessment was, perhaps, surprising (see Tables 7.3 and 7.4). However, this should not be questionable as depassivation cannot be detected by visual observation only because the appearance of coloured oxides may take some time (Alonso *et al*, 2000). Furthermore, as corrosion potentials varied over a relatively small range during the exposure, there was a reasonable agreement between corrosion potentials and rust indices made by visual assessment of recovered steel (see Tables 7.3 and 7.4).

As far as the influence of cement content on corrosion of steel in cracked (0.3 mm intersecting surface crack width) concrete is concerned, at a given time during the chloride exposure, there were no significant differences in corrosion potentials, corrosion currents (thus, corrosion rates) and rust indices of steel in concrete Mixes M5, M1 and M3*f*, see Tables 7.3. At the end of the test period, steel in Mixes M5, M1 and M3*f* gave corrosion potentials of -220, -318 and -312 mV and corrosion currents of 0.052, 0.122 and 0.046 $\mu A/cm^2$, respectively. The steel in all concrete types gave the same rust index (1). For cracked (intersecting) concrete, comparable corrosion potentials have been observed by previous researchers (Ohno *et al*, 1996; Li, 2000 and 2001). The slight differences between concrete types may be due to the variability associated with the corrosion test procedure. Indeed, these differences are small and can be ignored for practical purposes.

Similarly, the results indicated that the influence of surface crack width (intersecting) on the corrosion of steel in concrete (Mix M5) was insignificant. At a given time during the chloride exposure, there were no significant differences in corrosion potentials, corrosion currents (thus, corrosion rates) and rust indices of steel in concrete cracked to 0.1, 0.3 and 0.5 mm intersecting

surface crack widths (see Tables 7.4). At the end of the test, steel in concrete cracked to 0.1, 0.3 and 0.5 mm surface crack widths gave corrosion potentials of -219, -220 and -222 mV and corrosion currents of 0.067, 0.052 and 0.030 $\mu A/cm^2$, respectively. The same rust index (1) was found for the steel in all concrete types. It should be noted that for cracked (intersecting) concrete, similar corrosion activities have been reported by previous researchers (Ohno *et al*, 1996; Schiessel and Raupach, 1997). It is worth mentioning that the slight differences between concrete cracked to different intersecting surface crack widths may be attributed to the variability associated with the corrosion test procedure and the healing of cracks with salt crystals. Indeed, they can be ignored for practical purposes.

Therefore, it can be concluded that at w/c ratio 0.45;

- For cracked (intersecting) concrete (0.3 mm surface crack width) made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate, reduction in cement and water contents with the inclusion of limestone filler (M3*f*) to maintain the fines content equal to that of the Reference Mix (M1), or increasing cement and water contents with workability increase from 75 to 180 mm nominal slump (M5), led to negligible influences on the resistance of concrete to chloride-induced reinforcement corrosion compared to the Reference Mix (M1).
- For the concrete Mix M5, the intersecting surface crack width varying from 0.1 to 0.5 mm, had no influence on the resistance of concrete to chloride-induced reinforcement corrosion.

There are considerable differences in opinions about the influences of cracking on the corrosion of reinforcing steel in concrete. The results given in this chapter are in line with the suggestions of Gergely (1981) and Wilkins and Lawrence (1983). They have shown that corrosion initiation was not significantly affected by surface crack widths less than about 0.3 to 0.6 mm. Moreover, CEB (1989) and Broomfield (1997) suggest that the influence of intersecting cracks up to about 0.4 to 0.5 mm on corrosion is relatively small and any on-going corrosion is likely to come to a halt due to self-healing effects. This agrees with the results of the current study with corrosion potentials remaining approximately constant after reaching peak values in about 4 to 6 weeks.

The above results can probably be attributed to the chloride penetration and corrosion mechanisms in cracked (intersecting) concrete. Firstly, for chloride penetration, although there may be some influence of crack width on chloride penetration (see Section 7.2.1), it is unlikely that corrosion will be controlled by the availability of chlorides. Indeed, Francois and Arliguie (1999) showed that chloride penetration into beams with 0.5 mm maximum surface crack width (intersecting) was greater than that into beams with 0.2 mm maximum surface crack width (intersecting), but both beam types resulted in very similar corrosion activities. Secondly, for the most common corrosion mechanism in cracked (intersecting) concrete, the exposed portion of a bar normally acts as an

anode and the passive steel a cathode; the corrosion is controlled by the availability of oxygen and moisture, not at the crack, but in the sound concrete, and the electrical resistivity between the anode and the cathode (Beeby, 1978; ACI Committee 224.1R, 1993; Concrete Society, 1995). In other words, the corrosion is limited by the same factors as in uncracked concrete and there is a negligible effect of the intersecting crack width on corrosion.

However, it should be noted that in general, the intersecting crack width may affect corrosion initiation (Beeby, 1978; Ohno *et al*, 1996; Li, 2001), but does not influence subsequent propagation (Beeby, 1978; ACI Committee 224.1R, 1993; Concrete Society, 1995; Schiessel and Raupach, 1997; Francois and Arliguie; 1999). The observed results support this hypothesis if the corrosion initiation was very fast so that the influence of crack width on corrosion initiation was undetectable. Indeed, according to the measured corrosion potential values, it appears that this situation has occurred as corrosion initiated in about 4 to 5 weeks, regardless of the crack width for steel in the concrete Mix M5.

In addition, it should be noted that the principal factor affecting chloride-induced corrosion of steel in cracked (intersecting) concrete is w/c ratio and the degree of corrosion increases as the w/c ratio increases (Ohno *et al*, 1996; Schiessel and Raupach, 1997; Li, 2000 and 2001). Moreover, Li (2000) suggests that there is a negligible effect of cement type on chloride-induced corrosion of steel in cracked (intersecting) concrete. As mentioned earlier, the mechanisms associated with variation in cement content at fixed w/c ratio in controlling chloride-induced corrosion of steel in uncracked concrete (see Section 6.2.3), are also likely to influence that in cracked concrete. However, it appears that the influences of these mechanisms are not pronounced, probably due to shorter exposure periods, which allowed only corrosion initiation. In fact, longer exposure periods were not used to eliminate problems associated with healing of cracks with salt crystals. Therefore, overall, it can be concluded that the influence of variation in cement and water contents in equal proportion on the resistance of cracked (0.3 mm intersecting surface crack width) concrete to chloride-induced reinforcement corrosion is insignificant.

7.3 CONCLUSIONS

The conclusions given below can be drawn from the results in this chapter. They are based on concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate. These are for 28-day water-cured (20°C), reinforced concrete beam specimens under static loading conditions (with intersecting cracks), exposed to alternative 6 hours wetting (with 3.5% NaCl solution at 20°C to simulate sea water) and drying (20°C) cycles. Note that there is a discussion of the practical implications of these conclusions in Chapter 8.

7.3.1 Chloride Content

- For concrete with 0.3 mm surface crack width, reduction in cement and water contents in equal proportion with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix and increasing cement and water contents in equal proportion with workability increase, resulted in a slight increase and decrease in chloride penetration through the cracked zone, respectively, compared to the Reference Mix.

- For the cement-and-water-increased (in equal proportion) concrete mix with increased workability, chloride penetration through the cracked zones having surface crack widths of 0.1, 0.3 and 0.5 mm, was controlled by the crack width to a certain extent. However, it was not directly proportional to the surface crack width. The chloride penetration through the uncracked sections was significantly lower compared to that through cracked sections.

7.3.2 Chloride-Induced Corrosion

- For concrete with 0.3 mm surface crack width, reduction in cement and water contents in equal proportion with the inclusion of limestone filler to the maintain fines content equal to that of the Reference Mix, or increasing cement and water contents in equal proportion with workability increase, led to negligible influences on the resistance of concrete to chloride-induced reinforcement corrosion compared to the Reference Mix.

- For the cement and water increased (in equal proportion) concrete mix with increased workability, the surface crack width varying from 0.1 to 0.5 mm, had no influence on the resistance of concrete to chloride-induced reinforcement corrosion.

CHAPTER 8

OVERALL CONCLUSIONS, PRACTICAL IMPLICATIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

8.1 INTRODUCTION

The main findings of the experimental work have been considered at the end of each chapter. The aim of this chapter is to draw together the various stages of the project, consider the practical implications arising from the study and provide recommendations for further work.

Before reviewing the conclusions, it is worth briefly mentioning again the various stages of the project including their aims and objectives and, in particular, cement and aggregate types used.

Stage 1 was focused on investigating the effect of variation in cement and water contents in equal proportion, *i.e.* at fixed w/c ratio, on the fresh, engineering, permeation and durability properties of concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate.

Stage 2 was carried out to examine the effect of changing cement content at fixed w/c ratio on the resistance of uncracked concrete to carbonation-and-chloride-induced reinforcement corrosion. In addition to the corrosion, selected permeation properties of concrete and resistance of concrete to carbonation, chloride diffusion and chloride ingress were examined. The main cement type (PC, 42.5 N) was used with (i) natural gravel, (ii) granite and (iii) dolomitic magnesium limestone, and the main coarse aggregate type (dolomitic magnesium limestone) was combined with (i) 100% PC, (ii) 70% PC / 30% PFA and (iii) 50% PC / 50% GGBS.

Stage 3 was carried out to examine the effect of variation in cement content at fixed w/c ratio on the resistance of cracked (intersecting) concrete to chloride ingress and chloride-induced reinforcement corrosion using concrete made with PC, 42.5 N and dolomitic magnesium limestone coarse aggregate.

As mentioned earlier, for all these stages, a common approach was adopted to investigate the variation in cement content at fixed w/c ratio on a range of concrete properties. Initially, at a given w/c ratio, a Reference Mix was designed to have an average workability (a nominal slump of 75 mm) with no admixture. Its water content was governed by the characteristics of particular aggregate and cement types and was typically around 180 l/m^3. Thereafter, at fixed w/c ratio, cement (and, thus, water) content was reduced below the limits given in specifications (up to

a 40 l/m^3 water reduction) and a number of other mixes were designed. Moreover, to investigate the effect of maintaining the fines content (particles < 75 μm) of concrete at the Reference Mix level, with cement reduction, several other mixes were made with the inclusion of a limestone powder as part of the sand content. The workability of all cement-reduced mixes was maintained equal to that of the Reference Mix using a superplasticizing admixture. Furthermore, at a given w/c ratio, two other mixes were designed to examine the effect of increasing cement content (and hence a water content of typically up to about 200 l/m^3), giving higher workability (180 mm nominal slump), and the effect of raising workability from 75 to 180 mm nominal slump through the use of superplasticizer, but maintaining the cement and water contents at the Reference Mix level.

As indicated, PC, 42.5 N and dolomitic magnesium limestone coarse aggregate were used as the main cement and coarse aggregate type, respectively, during the project and, unless noted otherwise, the discussion in this chapter is based on concrete made with these materials.

8.2 OVERALL CONCLUSIONS

8.2.1 Fresh Properties

Workability

Regardless of the aggregate and cement type used, at fixed w/c ratio, it was possible to reduce the water content by up to 40 l/m^3 (and hence cement content) relative to the Reference Mix and to maintain the workability (75 mm nominal slump) with the use of superplasticizing admixture. However, the SP dosage required to maintain the workability increased with the water (and, thus, cement) reduction. The SP dosage was, however, not related to the fines content in the mix and, therefore, mixes with limestone filler to maintain the fines content equal to that of the Reference Mix, required similar SP dosages to those without filler. In addition, aggregate and cement type gave no clear influence on the SP dosage required to maintain the workability.

Cohesion and Finishability

All the Reference Mixes exhibited good cohesion and finishability characteristics. At a given w/c ratio, a water (and, thus, cement) reduction of up to 20 l/m^3 had no effect on the cohesion and finishability of fresh concrete compared to the Reference Mix, either with-or-without the fines content in the mix being maintained through the use of filler. However, a 40 l/m^3 water reduction resulted in a loss of cohesion and finishability and hence increased the likelihood of segregation and difficulties in achieving a smooth surface finish. This was partially offset by the inclusion of limestone filler. On the other hand, at fixed w/c ratio, raising workability using superplasticizer or increasing cement and water contents with increased workability, generally improved cohesion and finishability of concrete compared to the Reference Mix.

Air Content

At fixed w/c ratio, reduction in cement (and water) content, either with-or-without limestone filler to maintain the fines content equal to that of the Reference Mix, raising workability using superplasticizer or increasing cement and water contents with increased workability, led to no significant changes in air content in comparison to the Reference Mix.

Bleeding

At fixed w/c ratio, reduction in cement (and water) content delayed bleeding initiation and significantly reduced cumulative bleeding at a given time compared to the Reference Mix, potentially, giving beneficial effects to hardened concrete properties. This was more pronounced when the filler was included to maintain the fines content equal to that of the Reference Mix. However, when cement and water contents were increased in equal proportion with workability increase, bleeding tended to increase compared to the Reference Mix.

8.2.2 Engineering Properties

Compressive Strength

For a given w/c ratio and test age, the compressive strength generally increased with reduction in cement (and water) content, particularly when the filler was included in the mix to maintain the fines content at the Reference Mix level. Raising workability using superplasticizer and increasing cement and water contents with increased workability, led to a minor strength gain and almost no change in strength compared to the Reference Mix, respectively. However, it should be noted that the w/c ratio remained the main influencing factor for compressive strength, not the cement content.

Flexural Strength

In general, at a given w/c ratio, reduction in cement content had no adverse effect on the flexural strength. However, cement reduction and the inclusion of limestone filler to maintain the fines content at the Reference Mix level, resulted in slightly higher flexural strengths compared to the Reference Mix. Raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, had no influence on the flexural strength and a slight reduction, respectively, compared to the Reference Mix. In addition, a reduction in cement and water contents slightly reduced the flexural / compressive strength ratio and, therefore, there was a tendency for increase brittleness.

Static Modulus of Elasticity

The modulus of elasticity of concrete was largely influenced by the compressive strength and generally increased with reduction in cement and water contents at fixed w/c ratio, particularly

when limestone filler was included to maintain the fines content at the Reference Mix level. Thus, structures made with these mixes should have a better performance than those made with the Reference Mix, in terms of their resistance to deflection. At fixed w/c ratio, raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, resulted in a slight increase and decrease in modulus of elasticity, respectively, compared to the Reference Mix.

Load to Failure

The results obtained using the full stress / strain relationships were generally in agreement with the compressive strength and modulus of elasticity results. At fixed w/c ratio, reduction in cement (and water) content tended to increase the brittleness of concrete, particularly when limestone filler was included to maintain the fines content equal to that of the Reference Mix. Overall, it appears that increased compressive strength, modulus of elasticity and more brittle behaviour of cement-and-water-reduced concrete were linked to each other, particularly when the filler was included. However, increasing cement and water contents with increased workability led to only a minor change in the stress / strain characteristics of concrete compared to the Reference Mix.

Drying Shrinkage

At fixed w/c ratio, reduction in cement and water contents reduced drying shrinkage. This effect was slightly more pronounced when the filler was included to maintain the fines content at the Reference Mix level. Raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, led to a higher shrinkage compared to the Reference Mix. These effects appear to reflect the relative quantities of shrinkable and restraining material in concrete.

8.2.3 Permeation Properties

Capillary Porosity

For a given w/c ratio, the capillary porosity (which is not a permeation property, but influences the permeation properties) of concrete decreased with reduction in cement (and water) content, particularly when the filler was included in the mix to maintain the fines content at the Reference Mix level. This is beneficial since higher porosities with interconnected pores contribute to enhance the transport of fluids through concrete and influence deterioration rates. When cement and water contents were increased with workability increase, capillary porosity increased slightly compared to the Reference Mix. These effects were not influenced by the aggregate or cement type. However, at a given w/c ratio, for a given mix, capillary porosity increased with water absorption of aggregates. In addition, at a given w/c ratio, for a given mix, the use of PFA or GGBS with PC

reduced the capillary porosity of concrete compared to PC and the performance of concrete made with PC / GGBS was slightly better than that of PC / PFA.

Water Absorption and Initial Surface Absorption (ISA)

As expected, the water absorption and initial surface absorption of concrete closely followed the capillary porosity results, reflecting fewer pathways for absorption with cement (and water) reduction at fixed w/c ratio, particularly with the inclusion of filler to maintain the fines content at the Reference Mix level and, thus, potential benefits for durability of concrete. In addition, ISA results indicated that at fixed w/c ratio, the use of superplasticizer to raise workability slightly reduced ISA-10 compared to the Reference Mix.

Air Permeability

For a given w/c ratio, the changes occurring with variation in cement and water contents were essentially similar to those noted for capillary porosity, water absorption and ISA. These results also suggested that cement (and water) reduction at a given w/c ratio, particularly with the inclusion of the filler to maintain the fines content at the Reference Mix level, was likely to improve the concrete microstructure (in terms of permeability) and, consequently, durability.

8.2.4 Durability Properties

Carbonation Resistance

For a given w/c ratio, the carbonation resistance of water-cured (at 20°C for 28 days) concrete slightly decreased with cement and water reduction, particularly when the fines content was allowed to deplete. This may accelerate the depassivation of reinforcing steel in concrete with lower cement contents. However, this effect was partly offset by the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix. On the other hand, raising workability through the use of superplasticizer or increasing cement and water contents with increased workability, slightly improved the carbonation resistance compared to the Reference Mix. However, it should be noted that the cement content had little practical significance for the carbonation resistance of concrete compared to the w/c ratio, which was the main influencing factor.

Chloride Diffusion

At a given w/c ratio, reduction in cement (and water) content led to a slight reduction in chloride diffusion coefficient (determined using the potential difference method) and this effect was greatest when the filler was included to maintain the fines content at the Reference Mix level. This effect is likely to be beneficial as it will delay chloride penetration rates into the concrete and, consequently, the period to the breakdown of the protective passive layer surrounding the reinforcing steel.

Raising workability with the use of superplasticizer or increasing cement and water contents with increased workability, slightly increased the chloride diffusion coefficient compared to the Reference Mix. However, as for the carbonation resistance, the main influencing parameter on chloride diffusion was the w/c ratio and the variation in cement and water contents at fixed w/c ratio had little practical significance.

Sulfate Resistance

The results obtained for exposure up to 98 weeks showed that at fixed w/c ratio, the resistance of concrete to sulfate attack increased with reducing cement (and water) content and this effect was significant when the filler was included to maintain the fines content at the Reference Mix level. Raising workability through the use of superplasticizer or increasing cement and water contents with increased workability, slightly decreased sulfate resistance compared to the Reference Mix.

Freeze / Thaw Resistance

At fixed w/c ratio, reduction in cement and water contents improved the freeze / thaw resistance of concrete, however, when the filler was included to maintain the fines content equal to that of the Reference Mix, freeze / thaw resistance was reduced significantly compared to the Reference Mix. Raising workability through the use of superplasticizer and increasing cement and water contents with increased workability, increased the freeze / thaw resistance to a significant and limited extent, respectively, compared to the Reference Mix. Overall, it should be noted that the effect of cement content on freeze / thaw resistance of concrete was somewhat unclear. In normal practice, a minimum level of air-entrainment is specified for concrete exposed to freeze / thaw conditions in the presence of sodium chloride. Therefore, it should be recognised that these are plain concrete and that it is likely that with air-entrainment, any differences noted between concrete types would be expected to reduce.

Abrasion Resistance

At fixed w/c ratio, reduction in cement and water contents led to improved abrasion resistance. This effect was greatest when the filler was included to maintain the fines content at the Reference Mix level. Indeed, this is in line with observed compressive strength results and is beneficial to concrete as it improves the hardness of the surface zone. Raising workability through the use of superplasticizer led to a slight improvement in abrasion resistance in comparison to the Reference Mix, whilst a slightly reduced resistance was observed when cement and water contents were increased with workability increase.

8.2.5 Resistance of Concrete to Carbonation-Induced Reinforcement Corrosion

Carbonation Resistance

At fixed w/c ratio, the carbonation resistance of air-cured (at 20°C and 55% RH for 28 days) concrete tended to decrease with cement and water reduction, particularly when the fines content was allowed to deplete. However, this effect was partly offset by the inclusion of limestone filler to maintain the fines content at the Reference Mix level. Increasing cement and water contents with increased workability slightly improved the carbonation resistance compared to the Reference Mix.

At fixed w/c ratio, the changes occurring with variation in cement and water contents were, in the main, similar for concrete made with all aggregate types. However, for a given mix, concrete made with granite showed the highest resistance to carbonation but there was no significant difference between concrete made with natural gravel and dolomitic magnesium limestone.

At fixed w/c ratio, the changes occurring with variation in cement and water contents were not influenced by the cement type. However, for a given mix, carbonation resistance was influenced by cement type with both PC / PFA and PC / GGBS concrete giving higher carbonation rates than PC concrete and this was highest for PC / PFA. In addition, the effect of cement type on carbonation was more pronounced than the effect of cement content.

Overall, for air-cured concrete, cement (and water) reduction at fixed w/c ratio may accelerate carbonation-induced reinforcement corrosion initiation, particularly when the fines content is allowed to deplete. However, the effect of cement content is less pronounced and likely to have little practical significance compared to the influence of cement type and the best performance can be achieved using concrete containing good quality aggregates and PC.

Carbonation-Induced Corrosion

At fixed w/c ratio, reduction in cement and water contents with-or-without the inclusion of limestone filler to maintain the fines content at the Reference Mix level, or increasing cement and water contents with workability increase, had no influence on subsequent corrosion, once this had initiated. This behaviour was not influenced by the aggregate type and when relevant mixes (at fixed w/c ratio) were compared, there was no influence of the aggregate type on carbonation-induced reinforcement corrosion after initiation. Furthermore, the above behaviour was not influenced by the cement type, however, at fixed w/c ratio, for a given mix, both PC / PFA and PC / GGBS concrete gave higher corrosion rates than PC concrete with PC / GGBS tending to be the highest. In addition, the effect of cement content on corrosion rate was insignificant compared to the effect of cement type.

Overall, at fixed w/c ratio, variation in cement and water contents has no practical significance on carbonation-induced reinforcement corrosion after initiation, regardless of the aggregate and cement type used. In addition, the effect of cement content on corrosion rate is less pronounced compared to the influence of cement type. The use of PFA or GGBS with PC is likely to increase the corrosion rate compared to the use of PC alone.

8.2.6 Resistance of Concrete to Chloride-Induced Reinforcement Corrosion

Chloride Diffusion and Chloride Content at Cover Depth

At fixed w/c ratio, reduction in cement and water contents led to a minor reduction in chloride diffusion coefficient (determined using the concentration difference method). This effect was greatest when the filler was included to maintain the fines content at the Reference Mix level. Increasing cement and water contents with workability increase slightly increased the chloride diffusion coefficient compared to the Reference Mix.

The above effects were not influenced by the aggregate type. However, at fixed w/c ratio, for a given mix, aggregate type had a significant influence on the chloride diffusion with lowest diffusion coefficient obtained for concrete with aggregate of lowest absorption.

In addition, the effects noted above were not influenced by the cement type. However, at fixed w/c ratio, for a given mix, cement type greatly influenced the chloride diffusion with both PC / PFA and PC / GGBS concrete giving lower chloride diffusion coefficients compared to PC concrete and PC / GGBS tending to be the lowest. Moreover, the effect of cement type on chloride diffusion was more pronounced than the effect of cement content.

In general, at fixed w/c ratio, the build-up of water-soluble chlorides at the level of the steel for concrete made with different cement (and water) contents closely followed the chloride diffusion coefficient results, giving lower chloride contents with cement reduction, in particular with the inclusion of limestone filler, regardless of the aggregate and cement type used. However, at fixed w/c ratio, for a given mix, concrete with aggregate of lowest absorption and PC / PFA or PC / GGBS, particularly PC / GGBS gave the highest resistance to chloride penetration.

Overall, at fixed w/c ratio, cement (and water) reduction with the inclusion of filler to maintain the fines content at the Reference Mix level, is likely to delay chloride-induced reinforcement corrosion initiation. The best performance can be achieved using concrete containing good quality aggregates and PC / GGBS.

Chloride-Induced Corrosion

At fixed w/c ratio, reduction in cement and water contents and increasing cement and water contents with workability increase, led to a minor improvement and reduction in the resistance of concrete to chloride-induced reinforcement corrosion, respectively, compared to the Reference Mix. However, on a practical basis, these changes were insignificant. When the filler was included to maintain the fines content at the Reference Mix level, with cement reduction, corrosion activity was significantly reduced compared to the Reference Mix. These effects were not influenced by the aggregate type and there was no influence of this on chloride-induced reinforcement corrosion. Moreover, above-mentioned effects were unaffected by the cement type as well, however, at fixed w/c ratio, for a given mix, both PC / PFA and PC / GGBS concrete gave improved performances compared to PC concrete with PC / GGBS concrete performing the best.

Overall, regardless of the aggregate and cement type used, at fixed w/c ratio, variation in cement (and water) content has little practical significance on chloride-induced reinforcement corrosion, except cement (and water) reduction with the inclusion of filler to maintain the fines content at the Reference Mix level, which may significantly reduce corrosion activities. The use of PFA or GGBS with PC is likely to increase corrosion resistance compared to PC concrete.

8.2.7 Resistance of Cracked Concrete to Chloride-Induced Reinforcement Corrosion

Chloride Content

Under static loading conditions, for concrete with 0.3 mm surface crack (intersecting) width at fixed w/c ratio, reduction in cement and water contents with the inclusion of limestone filler to maintain the fines content equal to that of the Reference Mix and increasing cement and water contents with workability increase, led to a slight increase and decrease in chloride penetration through the cracked zone, respectively, compared to the Reference Mix. Chloride penetration through cracked (intersecting) sections was significantly higher than that through uncracked sections. In addition, this was controlled by the surface crack width varying from 0.1 to 0.5 mm, to a limited extent, but was not directly proportional to it. In general, cement content and surface crack width varying from 0.1 to 0.5 mm, appear to have little practical significance on chloride penetration through cracked sections and hence on corrosion initiation.

Chloride-Induced Corrosion

In general, reinforcement corrosion results of steel in cracked (intersecting) concrete followed the water-soluble chloride content results described above. Overall, under static loading conditions, cement content (at fixed w/c ratio) and surface crack (intersecting) width varying from 0.1 to 0.5 mm, are likely to have negligible practical influence on resistance of cracked concrete to chloride-induced reinforcement corrosion.

8.3 PRACTICAL IMPLICATIONS

8.3.1 Evaluation of Minimum Cement Content Requirement

Fresh and Hardened Properties of Concrete

In general, the results indicate that for a given set of mix constituents, at fixed w/c ratio, cement reduction below the given minimum cement contents in current specifications is not detrimental to concrete properties and may improve performance in some cases. In addition, the beneficial effects associated with cement reduction are generally more pronounced when the fines content of concrete is maintained. This implies that in most situations, there may be no need to specify minimum cement contents and, if specified, their values may be reconsidered compared to that currently in use. Furthermore, if a reduced or no minimum cement content is specified, consideration should be given to the specification of a minimum fines content to achieve a closed structure and to ensure the performance of concrete.

Resistance of Concrete to Reinforcement Corrosion

As far as corrosion initiation is concerned, for a given set of mix constituents, at fixed w/c ratio, cement reduction below the given minimum cement contents in current specifications may be slightly detrimental and beneficial in controlling carbonation-and-chloride-induced reinforcement corrosion initiation, respectively. In addition, the performance of cement-reduced concrete mixes is improved with the inclusion of limestone filler to maintain the fines content. However, it should be noted that the influence of cement content on these properties (and, indeed, permeation properties) is generally less pronounced and likely to have little practical significance compared to the influence of aggregate quality and cement type.

Furthermore, if corrosion process after initiation is considered, at fixed w/c ratio, cement content has no influence on carbonation-induced reinforcement corrosion. Similarly, this has insignificant influence on chloride-induced reinforcement corrosion. However, resistance of concrete to chloride-induced reinforcement corrosion is likely to improve when the filler is included to maintain the fines content with cement reduction at fixed w/c ratio.

Moreover, under static loading conditions, the corrosion results of cracked (intersecting) concrete, which represents real-life conditions, indicate that reduction in cement content below the current minimum values (at fixed w/c ratio) is likely to have negligible influence on resistance of concrete to chloride penetration and chloride-induced reinforcement corrosion.

Therefore, overall, it appears that there is little to justify the present minimum cement contents given in specifications to control carbonation-and-chloride-induced reinforcement corrosion in concrete. Indeed, the minimum cement content may be an unnecessary restriction on mix design.

Furthermore, it may be a mistake to pay too much attention to cement content in determining resistance of concrete to reinforcement corrosion, which is likely to be mainly influenced by the cement type (and w/c ratio).

In addition to the influence of cement content on reinforcement corrosion in concrete, as a further outcome of this research, the influence of crack width on reinforcement corrosion in concrete can be assessed. As the surface crack (intersecting) width varying from 0.1 to 0.5 mm, has no influence on chloride-induced reinforcement corrosion, there may be the possibility to increase current permissible crack width for reinforced concrete structures in aggressive environments from 0.3 to 0.5 mm, only where intersecting cracks are present in concrete structures under static loading conditions.

8.3.2 Influence of Cement Content on Concrete Performance Based on Equal Strength

Throughout this research, the effect of variation in cement content on various concrete properties was examined at fixed w/c ratio. As mentioned earlier, it was observed that at a given w/c ratio, the compressive strength generally increased with reduction in cement (and, thus, water) content, particularly when the filler was included to maintain the fines content. Therefore, it is interesting to see the influence of this strength advantage on durability properties when only a minimum strength grade is specified along with a minimum cement content. In other words, if all mixes were designed for the same strength, it would be useful to see the changes occurring to durability properties of concrete with variation in cement content. This was carried out for carbonation resistance and chloride diffusion as only these two durability properties were tested over a range of w/c ratios (in Stage 1). The results from the Reference Mix (M1), the cement-and-water-increased mix with raised workability (M5) and the cement-and-water-reduced (a 40 l/m^3 water reduction) mixes with (M3*f*) and without (M3) the inclusion of filler to maintain the fines content, were used for this analysis (these mixes were tested at all w/c ratios).

Carbonation Resistance

The mix limitations (characteristics) given in BS 8500: Part 1 (BSI, 2002) for the most severe carbonation environment, XC3/4 (moderate humidity or cyclic wet / dry), to achieve an intended working life of at least 50 years, include (for 25 mm minimum cover);

- minimum cement content 300 kg/m^3 (for 20 mm maximum aggregate size)
- minimum strength 40.0 N/mm^2
- maximum w/c ratio 0.55.

In Figure 8.1, the changes occurring to the w/c ratio and hence to the carbonation resistance of concrete with different cement contents are compared if a 40 N/mm^2 design strength is targeted.

These data are tabulated in Table 8.1. It is clear that the w/c ratio required to give 40 N/mm² concrete is highest at the lowest cement (and, thus, water) content, particularly when the filler is included to maintain the fines content (higher strength gain). For Mix M3*f*, the required w/c ratio increases by 0.07 (from 0.54 to 0.61) compared to the Reference Mix (M1), whilst an increase of 0.03 (from 0.54 to 0.57) is required for Mix M3. However, there is an insignificant difference between Mix M5 and the Reference Mix (M1). Overall, this indicates that the strength gains with cement (and, thus, water) reduction allow the w/c ratio of concrete to be increased. Indeed, this increases in the w/c ratio to maintain the strength of cement-and-water-reduced mixes will have an adverse effect on the carbonation resistance of concrete. When compared on a 40 N/mm² equal strength basis, the projected 20-week carbonation depths (28-day water-cured concrete at 20°C) of Mixes M3*f* and M3 are 25.5 and 21.0 mm, respectively, compared to 17.5 mm for the Reference Mix (46 and 20% increases), see Figure 8.1 and Table 8.1. It should be noted, however, that these adverse effects were less pronounced with cement reduction at fixed w/c ratio.

Therefore, it appears that specifying a minimum strength alone is insufficient to ensure the carbonation resistance of concrete. In fact, specifying both minimum strength and maximum w/c ratio for the present mix limitations given in specifications appears to be appropriate. In other words, the strength advantage observed at fixed w/c ratio with reduction in cement (and, thus, water) contents, particularly when the filler was included to maintain the fines content, should not be used to allow the use of higher w/c ratios on an equal strength basis.

In addition, it should be noted that the controlling parameter for achieving the given intended working life varies with variation in cement (and water) content. Mixes M3*f* and M3 tend to be controlled by w/c ratio (0.55), whilst for the Reference Mix, strength (40.0 N/mm²) remains the controlling parameter. Mix M6 is controlled by both w/c ratio (0.55) and strength (40.0 N/mm²) at the same time. However, it should be mentioned that for the same intended working life, BS 8500: Part 1 (BSI, 2002) allows changes to the maximum w/c ratio and minimum strength appropriately for different minimum covers.

Chloride Diffusion

The most severe chloride environments specified in BS 8500: Part 1 (BSI, 2002) are XS3 / XD3 (tidal, splash and spray exposure to seawater, or cyclic wet / dry exposure to other chlorides), which recommend the following mix limitations to achieve an intended working life of at least 50 years with 45 mm minimum cover;

- minimum cement content 360 kg/m³ (for 20 mm maximum aggregate size)
- minimum strength 40.0 N/mm²
- maximum w/c ratio 0.45.

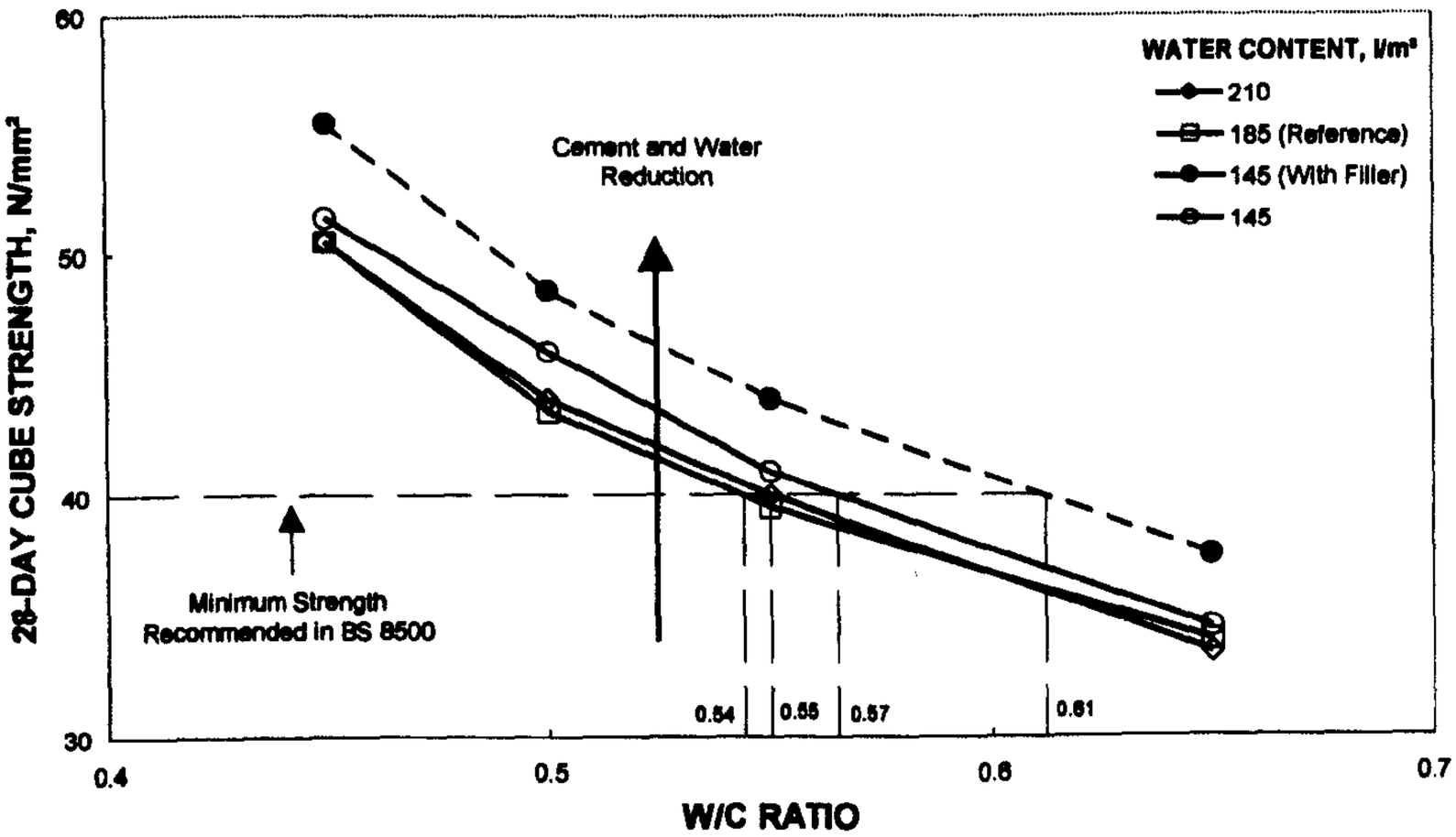
As for carbonation resistance, the changes occurring to the w/c ratio and hence to the chloride diffusion of concrete with different cement contents are compared in Figure 8.2 at a 40 N/mm² design strength. The results of this comparison are given in Table 8.1, together with the carbonation data. As discussed above, the strength gains observed at fixed w/c ratio with cement (and, thus, water) reduction, particularly when the fines content is maintained, allow the w/c ratio of concrete to be increased when compared on an equal strength basis. This increase in w/c ratio tends to influence the chloride diffusion of concrete adversely. Indeed, on a 40 N/mm² equal strength basis, the projected chloride diffusion coefficient (determined using the potential difference method) of Mix M3*f* (0.61 w/c ratio) is 25.3 x 10^{-7} cm²/s (13% increase) compared to 22.3 x 10^{-7} cm²/s for the Reference Mix (0.54 w/c ratio), see Figure 8.2 and Table 8.1. However, Mixes M3 (0.57 w/c ratio) and M5 (0.55 w/c ratio) result in only minor changes compared to the Reference Mix. On the other hand, it should be noted that at fixed w/c ratio, Mix M3*f* reduced the chloride diffusion coefficient by 7 to 10% compared to the Reference Mix.

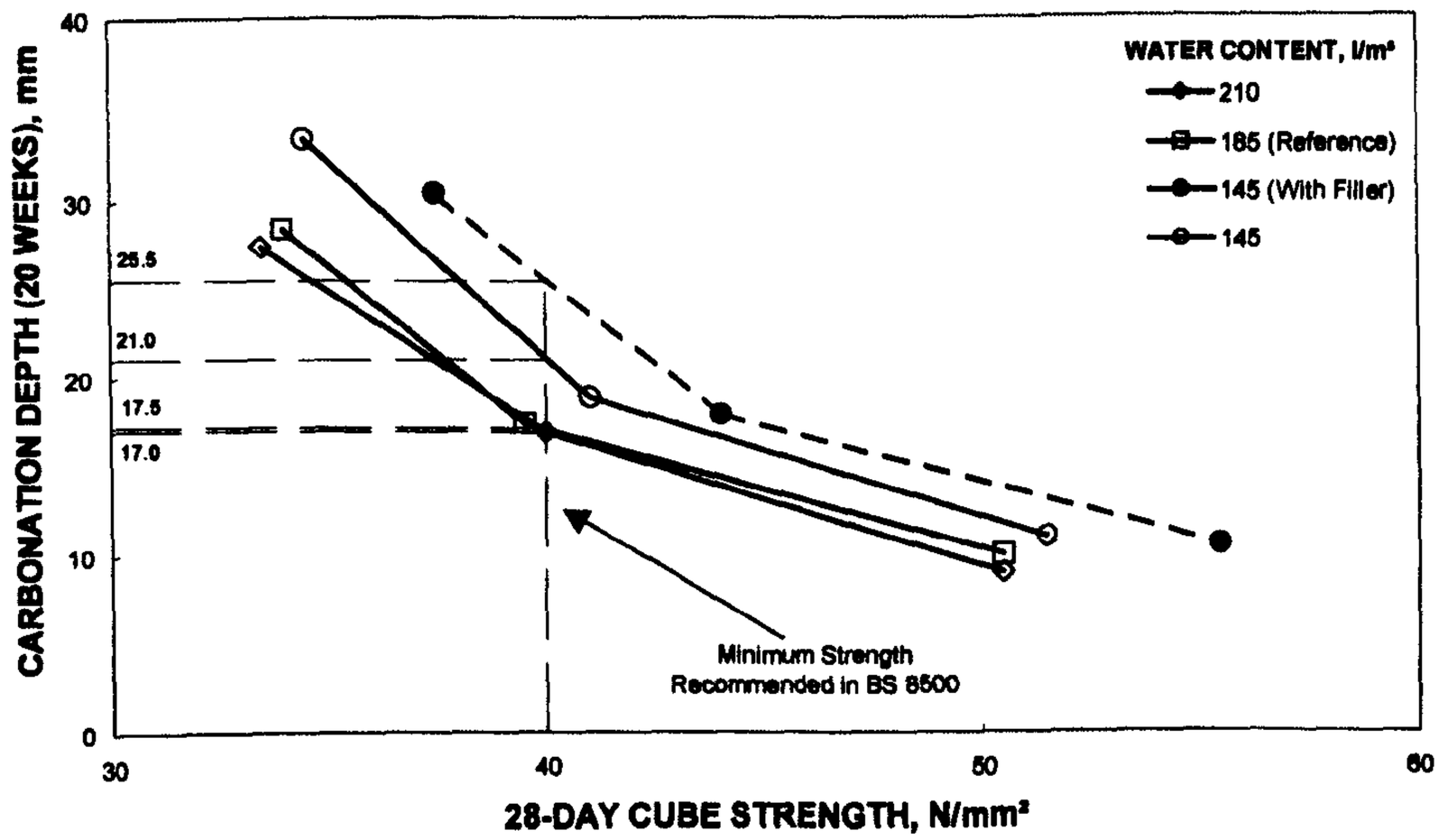
Therefore, the strength advantage observed at fixed w/c ratio with reduction in cement (and, thus, water) contents, particularly when the filler was included to maintain the fines content, should not be used to allow the use of higher w/c ratios on an equal strength basis for chloride environments as well. Moreover, as for carbonation resistance, this indicates that the present mix limitations given in specifications (specifying both minimum strength and maximum w/c ratio) are logical.

Table 8.1 Influence of cement content on carbonation and chloride resistance of concrete based on equal strength (40 N/mm²)

PROPERTY	INTERPOLATED VALUES				% OF M1			
	M5*	M1	M3*f*#	M3#	M5*	M1	M3*f*#	M3#
28-day cube strength, N/mm²	40.0	40.0	40.0	40.0	---	---	---	---
W/C ratio	0.55	0.54	0.61	0.57	102	100	113	106
Free water (nominal), l/m³	210	185	145	145	114	100	78	78
Cement (nominal), kg/m³	380	345	240	255	110	100	70	74
Carbonation depth (20 weeks), mm	17.0	17.5	25.5	21.0	97	100	146	120
Chloride diffusion coefficient (PD), cm²/s x 10^{-7}	23.6	22.3	25.3	22.4	106	100	113	100

All mixes contain PC, 42.5 N, dolomitic magnesium limestone and natural sand
*All mixes 75 mm nominal slump, except * 180 mm slump*
 # Superplastizer added to maintain workability
f Filler included to maintain fines content equal to that of M1





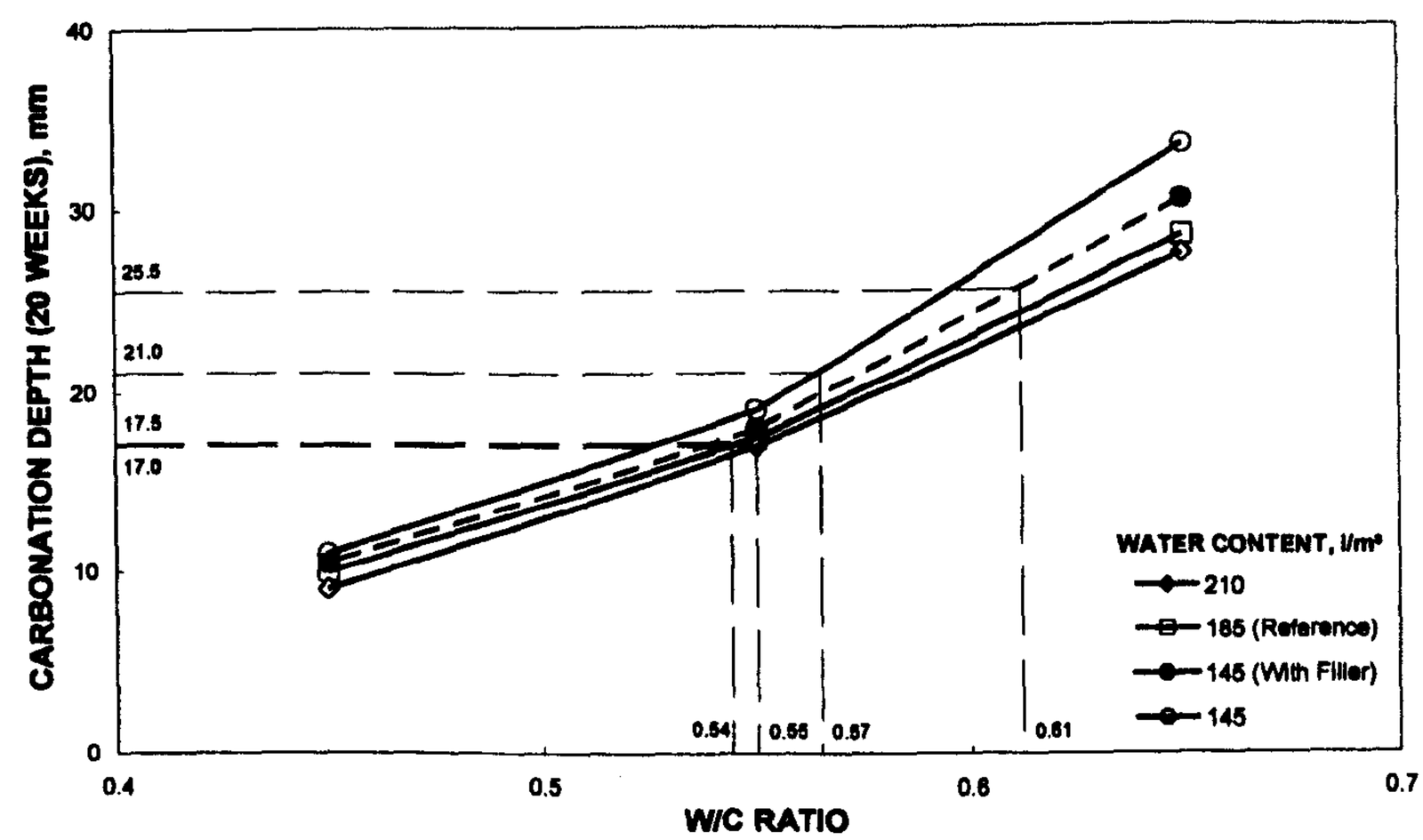
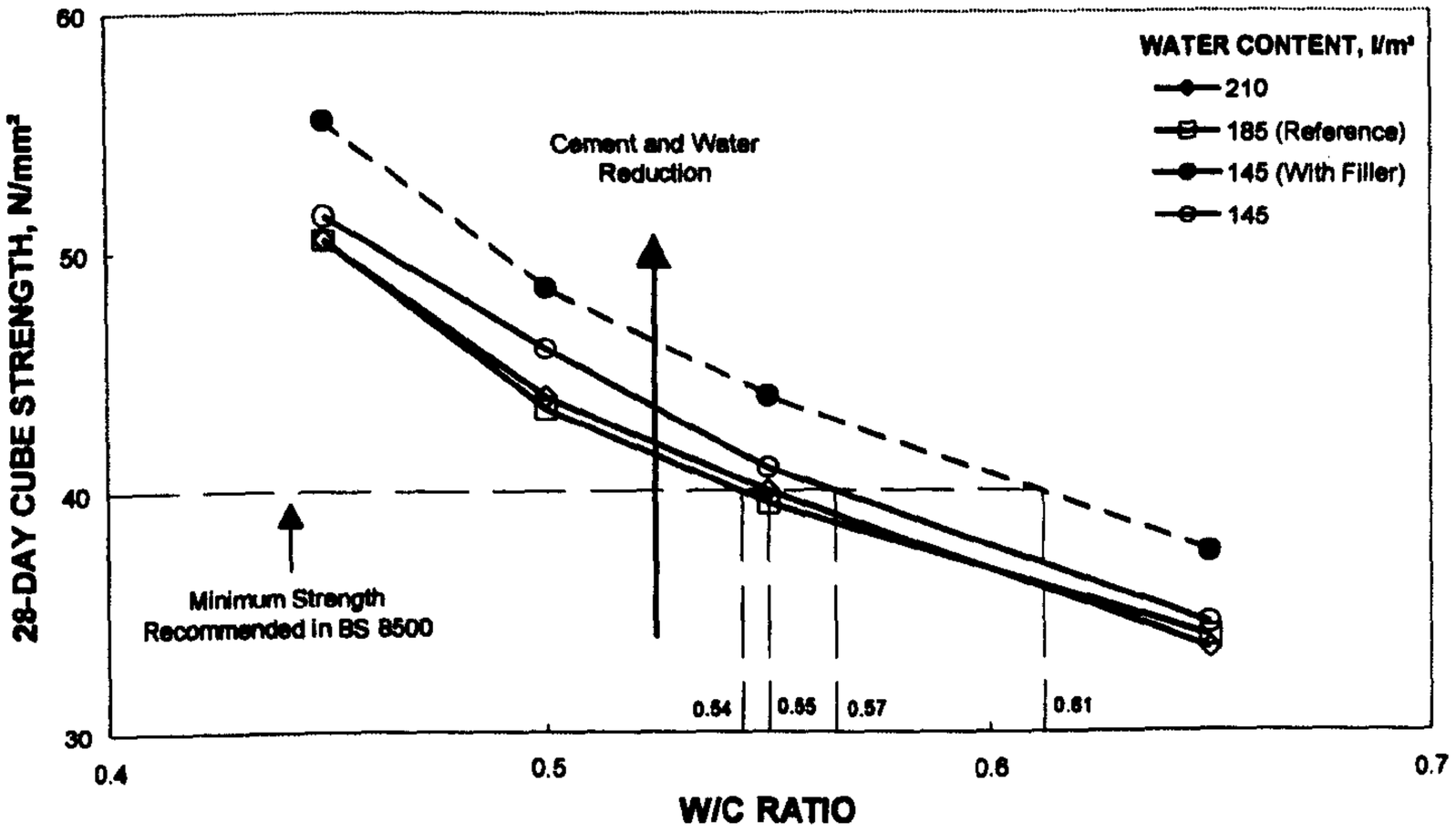
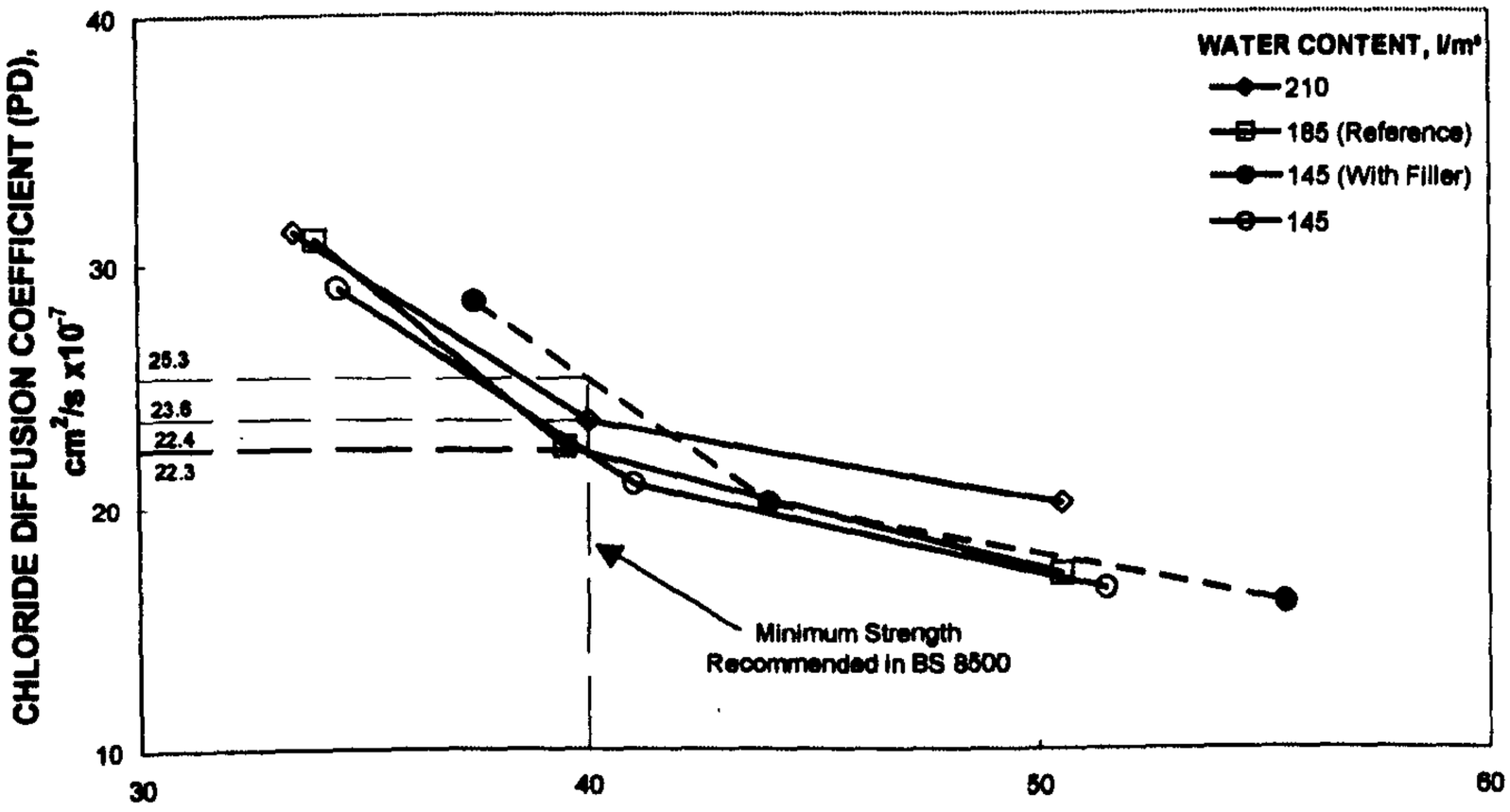


Figure 8.1 Changes in w/c ratio and carbonation resistance of concrete made with different cement contents at fixed w/c ratio when compared on 40N/mm² equal strength basis





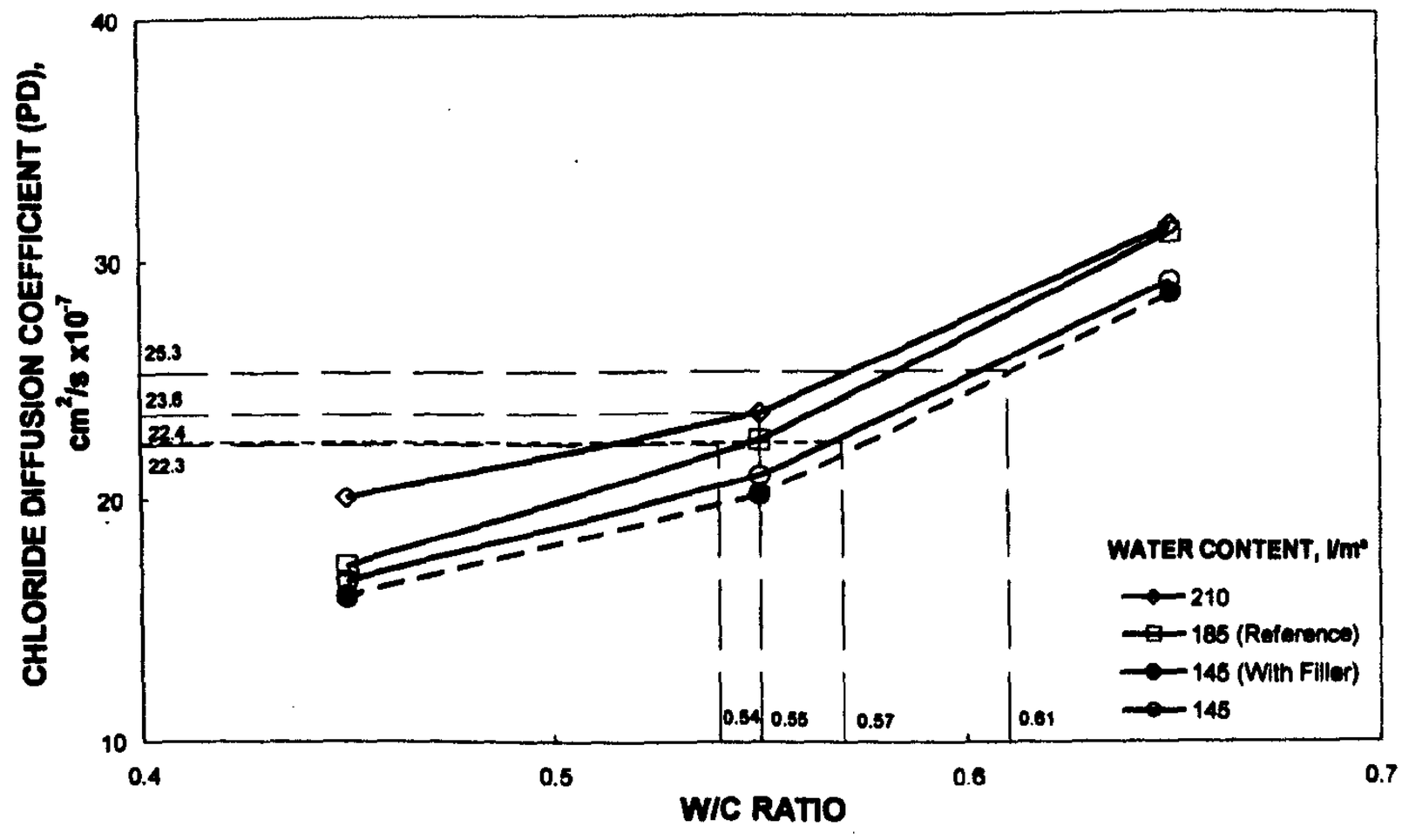


Figure 8.2 Changes in w/c ratio and chloride diffusion coefficient of concrete made with different cement contents at fixed w/c ratio when compared on 40N/mm² equal strength basis

In addition to the above implications, it should be noted that the controlling parameter for achieving the given intended working life tends to be w/c ratio (0.45) for all mixes, regardless of the cement content. However, as mentioned earlier, for the same intended working life, BS 8500: Part 1 (BSI, 2002) allows changes to the maximum w/c ratio and minimum strength appropriately for different minimum covers.

8.4 RECOMMENDATIONS FOR FURTHER RESEARCH

The work presented in this thesis demonstrated the feasibility of cement reduction at fixed w/c ratio below the given minimum cement contents in current specifications in terms of its influence on the fresh and hardened properties of concrete and, particularly, on the resistance of concrete to carbonation-and-chloride-induced reinforcement corrosion. As with most research work, the study was not able to address all relevant issues and, therefore, this section highlights the areas in which further research is required.

Mix Constituents

- Superplasticizing admixtures play an essential role in the process of reducing cement (and water) content at fixed w/c ratio for maintaining the workability of concrete. Although, there is a wide range of commercially available superplasticizing admixtures, only one was used throughout this study. In fact, the individual characteristics of different superplasticizing admixtures may have an influence on the performance of concrete. Therefore, this deserves further study to examine the possibility of replication of trends reported in this study with other superplasticizing admixtures.

- Air-entraining admixtures are widely used to improve the freeze / thaw resistance of concrete, particularly where the presence of sodium chloride is likely. As these admixtures are an important part of the modern concrete technology, there is a need to investigate the influence of variation in cement (and water) content with air-entraining admixtures at fixed w/c ratio on the performance of concrete, particularly freeze / thaw resistance.

- It was noted that the use of limestone powder as the filler to maintain the fines content of cement-reduced mixes at fixed w/c ratio, generally improved the fresh and hardened properties of concrete. Given this, it is important to investigate the possibility of using other fine materials having different physical and chemical characteristics as fillers.

- In this study, the effect of change in cement content at fixed w/c ratio on the resistance of uncracked concrete to reinforcement corrosion was investigated using three different cement and aggregate types. As reinforcement corrosion is likely to be mainly influenced by cement

type, it is necessary to extend this work using a range of commercially available cement types. In addition, the use of lightweight aggregates should be considered. Furthermore, it is also important to consider these different cement and aggregate types for cracked concrete.

Early-Age Thermal Cracking

- Concrete made with low cement contents reduces the heat of hydration hence the risk of early-age thermal cracking. In fact, this should play a vital role to resist the penetration of aggressive agents in liquid or gaseous form through concrete and hence to improve the durability and corrosion resistance of concrete. Therefore, the influence of variation in cement content at fixed w/c ratio on early-age thermal cracking of concrete should be examined using large concrete sections.

Alkali-Silica Reaction (ASR)

- Cement reduction at fixed w/c ratio reduces the total alkali content in the mix but, on the other hand, increases the reactive aggregate content. Clearly, the influence of variation in cement content at fixed w/c ratio on ASR should be investigated as surface cracks due to expansion associated with ASR are likely to affect the durability and corrosion resistance of concrete adversely.

Sulfate Resistance (Thaumasite Form of Sulfate Attack)

- It was noted that cement reduction (at fixed w/c ratio), particularly with the inclusion of limestone filler to maintain the fines content, improved the sulfate resistance of concrete. However, under cold wet conditions, the thaumasite form of sulfate attack could be possible when mixes contain carbonates. If aggregates contain carbonates, at fixed w/c ratio, cement reduction (increase in aggregate content) and/or inclusion of limestone powder could allow thaumasite formation in a suitable environment. Therefore, experimental work needs to be carried out to investigate this.

Resistance of Concrete to Reinforcement Corrosion

- Generally, small-scale specimens were used in this study. It is apparent that further investigations need to be carried out using large-scale specimens with different bar sizes, bar arrangements and covers, in order to identify and understand possible macro-cell effects associated with variation in cement content at fixed w/c ratio. In addition, continuation of this work using various curing conditions (low and high temperature water / air-curing, application of curing membranes *etc.*) and environmental conditions (temperatures and relative humidities) would be beneficial in relation to different climatic conditions.

- Given the significance of the chloride-induced reinforcement corrosion and due to time limitations, the effect of variation in cement content at fixed w/c ratio on resistance of cracked concrete to reinforcement corrosion was investigated only in chloride environments. However, in practice, reinforcement corrosion is possible in chloride free environments. It is, therefore, necessary to extend this work to examine carbonation-induced corrosion in cracked concrete.

- The work in this study was carried out using specimens with intersecting cracks. However, in outdoor conditions, cracks in concrete structures have different orientations and, indeed, this may affect the corrosion rate. Therefore, in addition to this, the influence of change in cement content at fixed w/c ratio on resistance of cracked concrete to reinforcement corrosion should be investigated using specimens with coincident cracks, which follow the line of the reinforcement.

- This work was limited only to reinforced concrete specimens. As there is a higher risk of corrosion of steel in pre-stressed concrete, it is important to extend this work using pre-stressed concrete specimens.

Multi-Aggressive Environments

- In this study, all durability and reinforcement corrosion (carbonation-and-chloride-induced) tests were carried out in separate, single exposure conditions. However, in practice, concrete structures are subjected to more than one aggressive process and, indeed, the performance of concrete is likely to be substantially poorer in these environments. Therefore, it is necessary to investigate the influence of cement content at fixed w/c ratio on the performance of concrete in multi-aggressive conditions (*e.g.* carbonation / chloride / sulfate exposure).

Natural Exposure Conditions

- There is a need for further work to be carried out in natural exposure conditions to investigate the influence of variation in cement and water contents in equal proportion on durability of concrete and its resistance to reinforcement corrosion. Indeed, this may assist in verifying the trends observed in this study and also enable the effectiveness of laboratory tests to estimate long-term performance of concrete to be evaluated.

Concrete Microstructure and Interfacial Transition Zone (ITZ)

- It is necessary to explain the beneficial effects obtained with cement reduction at fixed w/c ratio, particularly when limestone filler is included to maintain the fines content. In addition, the observed differences between concrete made with different aggregate and

cement types need to be explained. These issues require a microscopic analysis of concrete and characterisation of the interfacial transition zone (ITZ) between cement paste and aggregate particles.

REFERENCES

Al-Amoudi, O S B, Rasheeduzzafar and Maslehuddin, M. 1991. Carbonation and Corrosion of Rebars in Salt Contaminated OPC/PFA Concretes. Cement and Concrete Research, Vol 21, pp 38-50.

Ali, A. 1996. Superplasticisers in Concrete: A Review. Building Research Establishment, Watford, UK.

Alonso, C, Andrade, C and Gonzalez, J A. 1988. Relation between Resistivity and Corrosion Rate of Reinforcements in Carbonated Mortar Made with Several Cement Types. Cement and Concrete Research, Vol 18, No 5, pp 687-698.

Alonso, C, Andrade, C, Castellote, M and Castro, P. 2000. Chloride Threshold Values to Depassivate Reinforcing Bars Embedded in a Standardized OPC Mortar. Cement and Concrete Research, Vol 30, pp1047-1055.

American Concrete Institute (ACI). Detroit, USA.

ACI Committee 201.2R - 92. 1992. Guide to Durable Concrete.

ACI Committee 222R - 96. 1996. Corrosion of Metals in Concrete.

ACI Committee 224R - 90. 1990. Control of Cracking in Concrete Structures.

ACI Committee 224.1R - 93. 1993. Causes, Evaluation and Repair of Cracks in Concrete Structures.

ACI Committee 301 - 99. 1999. Specifications for Structural Concrete.

ACI Committee 318/318R - 99. 1999. Building Code Requirements for Structural Concrete and Commentary.

ACI Committee 345R - 91. 1991. Guide for Concrete Highway Bridge Deck Construction.

American Society for Testing and Materials (ASTM). Philadelphia, USA.

ASTM C 232 - 99. 1999. Standard Test Methods for Bleeding of Concrete.

ASTM C 876 - 91. 1991. Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete.

Andrade, C and Page, C L. 1986. Pore Solution Chemistry and Corrosion in Hydrated Cement Systems Containing Chloride Salts: A Study of Cation Specific Effects. British Corrosion Journal, Vol 21, No 1, pp 49-53.

Andrade, C, Alonso, C and Gonzalez, J A. 1990. An Initial Effort to Use the Corrosion Rate Measurements for Estimating Rebar Durability. In: Corrosion Rates of Steel in Concrete, Edited by N Berke, V Whiting and D Whiting. ASTM Special Technical Publication, 1065, pp 3–16.

Andrade, C, Castellote, M, Cervigon, D and Alonso, C. 1996. Influence of External Concentration and Testing Time on Chloride Diffusion Coefficient Values of Steady and Non-Steady Migration Experiments. In: Corrosion of Reinforcement in Concrete Construction, Edited by C L Page, P B Bamforth and J W Figg. Proceedings of the 4th International Symposium, Cambridge, UK, July, pp 76-87.

Arup, H. 1983. The Mechanism of the Protection of Steel by Concrete. In: Corrosion of Reinforcement in Concrete Construction, Edited by A P Crane. Ellis Horwood, London, UK, June, pp 59-78.

Arya, C and Xu, Y. 1995. Effect of Cement Type on Chloride Binding and Corrosion of Steel in Concrete. Cement and Concrete Research, Vol 25, No 4, pp 893-902.

Associated Portland Cement Manufacturers. 1921. Everyday Uses of Portland Cement. Forth Edition, London, UK.

Basheer, P A M, Montgomery, F R and Long, A E. 1994. Factorial Experimental Design for Concrete Durability Research. Proceedings of the Institution of Civil Engineers: Structures and Buildings, Vol 104, No 4, pp 449-462.

Beeby, A W. 1978. Corrosion of Reinforcing Steel in Concrete and Its Relation to Cracking. The Structural Engineer, Vol 56A, No 3, Mar, pp 77-81.

Beeby, A W. 1979. Concrete in the Oceans – Cracking and Corrosion. Cement and Concrete Association, Technical Report No 2, CIRIA/EG, Slough, UK.

Bennison, A W. 1984. The Repair and Protection of Reinforced Concrete. Corrosion Prevention and Control, Vol 31, No 3, pp 5-10.

Bentur, A, Diamond, S and Berke, N S. 1997. Steel Corrosion in Concrete: Fundamentals and Civil Engineering Practice. E & FN Spon, London, UK, 201pp.

Berman, H A. 1972. Determination of Low Levels of Chlorides of Hardened Portland Cement Mortar and Concrete. Journal of Materials, No 3, pp 330-335.

Bissonnette, B, Pierre, P and Pigeon, M. 1999. Influence of Key Parameters on Drying Shrinkage of Cementitious Materials. Cement and Concrete Research, Vol 29, No 10, pp 1655-1662.

BRE, 1995. Carbonation of Concrete and Its Effects on Durability. BRE Digest 405, Building Research Establishment, Watford, UK, 8pp.

BRE, 1996. Sulfate and Acid Resistance of Concrete in the Ground. BRE Digest 363, Building Research Establishment, Watford, UK, 12pp.

Brekos, V. 2000. Binary and Ternary Cement Influences on the Significance of Cement Content in Concrete Construction. MSc Thesis, University of Dundee, UK.

British Standards Institution (BSI). London, UK.

BS 12. 1996. Specification for Portland Cement.

BS 882. 1992. Specification for Aggregates from Natural Sources for Concrete.

BS 1881. 1983. Testing Concrete – Part 106. Methods for Determination of Air Content of Fresh Concrete.

BS 1881. 1983. Testing Concrete – Part 107. Method for Determination of Density of Compacted Fresh Concrete.

BS 1881. 1983. Testing Concrete – Part 108. Method for Making Test Cubes from Fresh Concrete.

BS 1881. 1983. Testing Concrete – Part 109. Method for Making Test Beams from Fresh Concrete.

BS 1881. 1983. Testing Concrete – Part 110. Method for Making Test Cylinders from Fresh Concrete.

BS 1881. 1983. Testing Concrete – Part 111. Method of Normal Curing of Test Specimens (20°C Method).

BS 1881. 1983. Testing Concrete – Part 116. Method for Determination of Compressive Strength of Concrete Cubes.

BS 1881. 1983. Testing Concrete – Part 118. Method for Determination of Flexural Strength.

BS 1881. 1983. Testing Concrete – Part 121. Method for Determination of Static Modulus of Elasticity in Compression.

BS 1881. 1988. Testing Concrete – Part 124. Methods for Analysis of Hardened Concrete.

BS 1881. 1986. Testing Concrete – Part 125. Methods for Mixing and Sampling Fresh Concrete in the Laboratory.

BS 1881. 1996. Testing Concrete – Part 208. Recommendations for the Determination of the Initial Surface Absorption of Concrete.

BS 3148. 1980. Methods of Test for Water for Making Concrete (Including Notes on the Suitability of the Water).

BS 3892. 1997. Pulverized-Fuel Ash – Part 1. Specification for Pulverized-Fuel Ash for Use with Portland Cement.

BS 4449. 1997. Specification for Carbon Steel Bars for the Reinforcement of Concrete.

BS 5328. 1997. Concrete - Part 1. Guide to Specifying Concrete.

BS 5400. 1990. Steel, Concrete and Composite Bridges - Part 4. Code of Practice for Design of Concrete Bridges.

BS 6349. 2000. Maritime Structures - Part 1. Code of Practice for General Criteria.

BS 6699. 1992. Ground Granulated Blastfurnace Slag for Use with Portland Cement.

BS 7979. 2001. Specification for Limestone Fines for Use with Portland Cement.

BS 8007. 1987. Code of Practice for Design of Concrete Structures for Retaining Aqueous Liquids.

BS 8110. 1985 (Updated 1997). Structural Use of Concrete - Part 1. Code of Practice for Design and Construction.

BS 8110. 1985. Structural Use of Concrete - Part 2. Code of Practice for Special Circumstances.

BS 8500. 2002. Concrete - Part 1. Complementary British Standard to BS EN 206-1 - Method of Specifying and Guidance for the Specifier.

BS EN 197 – 1. 2000. Cement - Part 1. Composition, Specification and Conformity Criteria for Common Cements.

BS EN 206 - 1. 2001. Concrete - Part 1. Specification, Performance, Production and Conformity.

BS EN 934 - 2. 2001. Admixtures for Concrete, Mortar and Grout - Part 2. Concrete Admixtures – Definitions, Requirements, Conformity, Marking and Labelling.

BS EN 12350 – 2. 2000. Testing Fresh Concrete - Part 2. Slump Test.

CP 110. 1972. Code of Practice for the Structural Use of Concrete.

CP 114. 1957. The Structural Use of Reinforced Concrete in Buildings.

CP 114.100. 1950. Suspended Concrete Floors and Roofs.

CP 115. 1959. The Structural Use of Prestressed Concrete in Buildings.

CP 116. 1965. The Structural Use of Precast Concrete.

Broomfield, J P. 1997. Corrosion of Steel in Concrete. E & FN Spon, London, UK, 240pp.

Brown, R D. 1982. Design Prediction of the Life of Reinforced Concrete in Marine and Other Chloride Environments. Durability of Building Materials, Vol 3, Elsevier Scientific Publishing Company, Amsterdam, Netherlands.

Browne, R D. 1985. Practical Considerations in Producing Durable Concrete - Improvement of Concrete Durability. ICE Seminar, London, pp 97-130.

Buenfeld, N R and Newman, J B. 1987. Examination of Three Methods for Studying Ion Diffusion in Cement Pastes, Mortars and Concrete. Materials and Structures, Vol 20, pp 3-10.

Buenfeld, N R and Okundi, E. 1998. Effect of Cement Content on Transport in Concrete. Magazine of Concrete Research, Vol 50, No 4, Dec, pp 339-351.

CEB. 1989. Durable Concrete Structures - Design Guide - Second Edition. Thomas Telford, London, UK, 112pp.

Chan, Y N. 1988. Near Surface Characteristics and Durability of Concrete. Internal Report, University of Dundee, UK.

Chaplin, R G. 1990. The Influence of GGBS and PFA Additions on the Abrasion Resistance of Industrial Concrete Floors. British Cement Association, Slough, UK, 64pp.

Collins, A R. 1950. The Principles of Making High-Strength Concrete. Civil Engineering and Public Works Review, Vol 45, No 524, Feb, pp 110-112.

Concrete Society. 1991. The Use of GGBS and PFA in Concrete - Technical Report No 40. The Concrete Society, Slough, UK, 142pp.

Concrete Society. 1995. The Relevance of Cracking in Concrete to Corrosion of Reinforcement – Technical Report No 44. The Concrete Society, Slough, UK, 32pp.

Concrete Society. 1996. Developments in Durability Design and Performance-Based Specification of Concrete – Discussion Document CS 109. The Concrete Society, Slough, UK, 69pp.

Concrete Society. 1999. The Influence of Cement Content on the Performance of Concrete – Discussion Document CS 125. The Concrete Society, Crowthorne, UK, 48pp.

Concrete Society. 2000. Diagnosis of Deterioration in Concrete Structures – Identification of Defects, Evaluation and Development of Remedial Action - Technical Report No 54. The Concrete Society, Crowthorne, UK, 72pp.

Constantinou, A G and Scrivener, K L. 1995. The Corrosion of Steel Reinforcement in Carbonated Concrete under Different Humidity Regimes. Proceedings of the Materials Research Society Symposium, Vol 370, pp 471-478.

Costa, A and Appleton, J. 1999. Chloride Penetration into Concrete in Marine Environment – Part I: Main Parameters Affecting Chloride Penetration. Materials and Structures, Vol 32, May, pp 252-259.

Crank, J. 1975. The Mathematics of Diffusion – 2nd Edition. Oxford University Press, 414pp.

Daniels, F and Alberty, R. 1975. Physical Chemistry – 4th Edition. Wiley, New York, 687pp.

De Schutter, G. 1999. Quantification of the Influence of Cracks in Concrete Structures on Carbonation and Chloride Penetration. Magazine of Concrete Research, Vol 51, No 6, Dec, pp 427-435.

Detwiler, R J and Tennis, P D. 1996. The Use of Limestone in Portland Cement: A State-of-the-Art-Review. RP 118, Portland Cement Association, Illinois, 38pp.

Dewar, J D. 1999. Computer Modelling of Concrete Mixtures. E & FN Spon, London, UK.

Dhir, R K, Jones, M R and Munday, J G L. 1985. A Practical Approach to Studying Carbonation of Concrete. Concrete, Vol 19, No 10, Oct, pp 32-34.

Dhir, R K. 1986. Pulverized-Fuel Ash. In: Cement Replacement Materials (Chapter 7), Edited by R N Swamy. Surrey University Press, UK, pp 197-255.

Dhir, R K, Tham, K and Dransfield, J. 1987a. Durability of Concrete with a Superplasticizing Admixture. In: Concrete Durability, Edited by J M Scanlon. ACI SP - 100, Vol 1, American Concrete Institute, Detroit, USA, pp 741-764.

Dhir, R K, Hewlett, P C and Chan, Y N. 1987b. Near-Surface Characteristics of Concrete: Assessment and Development of In Situ Test Methods. Magazine of Concrete Research, Vol 39, No 141, Dec, pp 183-195.

Dhir, R K, Hewlett, P C and Chan, Y N. 1989a. Near Surface Characteristics of Concrete: Intrinsic Permeability. Magazine of Concrete Research, Vol 41, No 147, pp 87-97.

Dhir, R K, Hewlett, P C and Chan, Y N. 1989b. Near-Surface Characteristics of Concrete: Prediction of Carbonation Resistance. Magazine of Concrete Research, Vol 41, No 148, pp 137-143.

Dhir, R K, Jones, M R, Ahmed, H E H and Seneviratne, A M G. 1990a. Rapid Estimation of Chloride Diffusion Coefficient in Concrete. Magazine of Concrete Research, Vol 42, No 152, Sep, pp 177-185.

Dhir, R K, Jones, M R and Ahmed, H E H. 1990b. Determination of Total and Soluble Chlorides in Concrete. Cement and Concrete Research, Vol 20, pp 579-590.

Dhir, R K, Hewlett, P C and Chan, Y N. 1991. Near Surface Characteristics of Concrete: Abrasion Resistance. Materials and Structures, Vol 24, No 140, pp 122-128.

Dhir, R K, Jones, M R and McCarthy, M J. 1992. Pulverized - Fuel Ash Concrete: Carbonation - Induced Reinforcement Corrosion Rates. Proceedings of the Institution of Civil Engineers: Structures and Buildings, Vol 94, Aug, pp 335-342.

Dhir, R K and Harrison, T A. 1993. Concrete for Durable Concrete Construction. Seminar for Hong Kong Government Civil Engineering Department, Nov, 100pp.

Dhir, R K, Jones, M R and McCarthy, M J. 1995. PFA Concrete: Chloride - Induced Reinforcement Corrosion. Magazine of Concrete Research, Vol 46, No 169, Dec, pp 269-277.

Dhir, R K and Jackson, N. 1996. Properties of Hardened Concrete. In: Civil Engineering Materials - Fifth Edition (Chapter 14), Edited by N Jackson and R K Dhir. Macmillan Press Limited, UK, pp 210-235.

Dhir, R K, Jones, M R and McCarthy, M J. 1996. Binder Content Influences on Chloride Ingress in Concrete. Cement and Concrete Research, Vol 26, No 12, pp 1761-1766.

Dhir, R K, Jones, M R and Ng, S L D. 1998. Prediction of Total Chloride Content Profile and Concentration / Time - Dependent Diffusion Coefficients for Concrete. Magazine of Concrete Research, Vol 50, No 1, Mar, pp 37-48.

Dias, W P S. 1993. Durability Indicators of OPC Concrete Subject to Wick Action. Magazine of Concrete Research, Vol 45, No 165, pp 263-274.

Dignan, M. 2000. Mix Design Limitations for Concrete Made with EN 197-1 Cements. MSc Thesis, University of Dundee, UK.

Erntroy, H C and Shacklock, B W. 1955. Design of High-Strength Concrete Mixes. Edited by R P Andrew. Proceedings of a Symposium on Mix Design and Quality Control of Concrete, Cement and Concrete Association, London, UK, May, pp 55-73.

Everett, L H and Treadaway, K W J. 1980. Deterioration Due to Corrosion in Reinforced Concrete. Building Research Establishment, Information Paper, IP 12/80, Aug, 4pp.

European Committee for Standardisation (CEN). Brussels, Belgium.

pr EN / TC 51. 1994. Draft. Test Methods for the Freeze - Thaw Resistance of Concrete – Tests with Water or with Sodium Chloride Solution. Part 1: Scaling. Reference Method A (Slab Test).

pr EN 12620. 2000. Draft. Aggregates for Concrete Including Those for Use in Roads and Pavements.

Figg, J W and Marsden, A F. 1984. Development of Inspection Techniques for Reinforced Concrete: A State of the Art Survey of Electrical Potential and Resistivity Measurements for Use Above Water Level. Concrete in the Oceans Technical Report No 10, Offshore Technology Report, OTH-84-205.

Francois, R and Arliguie, G. 1999. Effect of Microcracking and Cracking on the Development of Corrosion in Reinforcement Concrete Members. Magazine of Concrete Research, Vol 51, No 2, Apr, pp 143-150.

Gaynor, R. 1987. Understanding Chloride Percentages, Corrosion, Concrete and Chlorides. Edited by F W Gibson. ACI SP – 102, American Concrete Institute, Detroit, USA, pp 161-165.

Gergely, P. 1981. Role of Cover and Bar Spacing in Reinforced Concrete. In: Significant Developments in Engineering Practice and Research: A Tribute to C P Seiss. ACI SP – 72, American Concrete Institute, Detroit, USA, pp 133-147.

Glass, G K, Page, C L and Short, N R. 1991. Factors Affecting the Corrosion Rate of Steel in Carbonated Mortars. Corrosion Science, Vol 32, No 12, pp 1283-1294.

Glass, G K and Buenfeld, N R. 1997. The Presentation of the Chloride Threshold Level for Corrosion of Steel in Concrete. Corrosion Science, Vol 39, No 5, pp 1001-1013.

Glass, G K, Reddy, B and Buenfeld, N R. 2000. The Participation of Bound Chloride in Passive Film Breakdown on Steel in Concrete. Corrosion Science, Vol 42, No 11, pp 2013-2021.

Gonzalez, J A, Feliu, S, Rodriguez, P, Ramirez, E, Alonso, C and Andrade, C. 1996. Some Questions on the Corrosion of Steel in Concrete Part I : When, How and How Much Steel Corrodes. Materials and Structures, Vol 29, Jan-Feb, pp 40-46.

Gouda, V K. 1970. Corrosion and Corrosion Inhibition of Reinforcing Steel. British Corrosion Journal, Vol 5, pp 198–203.

Gouda, V K and Halaka, W Y. 1970. Corrosion and Corrosion Inhibition of Reinforcing Steel. British Corrosion Journal, Vol 5, pp 204–208.

Hamada, M. 1968. Neutralization (Carbonation) of Concrete and Corrosion of Reinforcing Steel. Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, pp 343-363.

Hansen, W and Almudaiheem, J A. 1987. Ultimate Drying Shrinkage of Concrete – Influence of Major Parameters. ACI Materials Journal, Vol 84, No 3, May-Jun, pp 217-223.

Hansson, C M and Sorensen, B. 1988. The Threshold Concentration of Chloride in Concrete for Initiation of Reinforcement Corrosion. In: Corrosion Rates of Steel in Concrete, Edited by N Berke, V Whiting and D Whiting. ASTM Special Technical Publication, 1065, pp 3–16.

Harrison, T A. 1997. The Role of Minimum Cement Content in the Achievement of Durable Concrete. ACT Course Lecture Notes, Imperial College of Science, Technology and Medicine, London, UK, 7th March, 28pp.

Hausmann, D A. 1967. Steel Corrosion in Concrete – How Does It Occur? Materials Protection, Vol 6, pp 19-23.

Hawkins, C and McKenzie, M. 1996. Environmental Effects on Reinforcement Corrosion Rates. In: Corrosion of Reinforcement in Concrete Construction, Edited by C L Page, P B Bamforth and J W Figg. Proceedings of the 4th International Symposium, Cambridge, UK, July, pp 166-175.

Hillier, S R, Sangha, C M, Plunkett, B A and Walden, P J. 2000. Effect of Concrete Curing on Chloride Ion Ingress. Magazine of Concrete Research, Vol 52, No 5, Oct, pp 321-327.

Ho, D W S and Lewis, R K. 1983. Carbonation of Concrete Incorporating Fly Ash or a Chemical Admixture. Proceedings of the 1st International Conference on the Use of Fly Ash, ACI SP – 79, pp 333-336.

Hobbs, D W. 1972. The Compressive Strength of Concrete: A Statistical Approach to Failure. Magazine of Concrete Research, Vol 24, No 80, Sep, pp 127-138.

Hobbs, D W. 1998. Minimum Requirements for Durable Concrete: Carbonation-and-Chloride-Induced Corrosion, Freeze-Thaw Attack and Chemical Attack. British Cement Association, Crowthorne, UK, 172pp.

Hobbs, D W. 1999. Aggregate Influence on Chloride Ion Diffusion into Concrete. Cement and Concrete Research, Vol 29, No 12, pp 1995-1998.

Hobbs, D W. 2001. Dundee Work on Cement Content and Coarse Aggregate Type. Private Communication, 28th February, 1pp.

Hong, K and Hooton, R D. 1999. Effect of Cyclic Chloride Exposure on Penetration of Concrete Cover. Cement and Concrete Research, Vol 29, pp 1379-1386.

Hope, B B and Ip, A K C. 1987. Chloride Corrosion Threshold in Concrete. ACI Materials Journal, Vol 84, No 4, Jul-Aug, pp 306-314.

Hope, B B and Ip, A K C. 1987. Corrosion of Steel in Concrete Made with Slag Cement. ACI Materials Journal, Vol 84, No 6, Nov-Dec, pp 525-531.

Hughes, B P and Ash, J E. 1968. The Effect of Mix Proportions and Aggregate Dust upon the Compressive Strength of Concrete. Magazine of Concrete Research, Vol 20, No 63, Jun, pp 77-84.

Hussain, S E and Rasheeduzzafar. 1994. Corrosion Resistance Performance of Fly Ash Blended Cement Concrete. ACI Materials Journal, Vol 91, No 3, May-Jun, pp 264-272.

Inoue, Y, Asano, S and Yamagiwa, Y. 1970. On the Carbonation of Cement Pastes Using Several Curing Methods. Review of the 24th General Meeting, Technical Session, Cement Association of Japan, Tokyo, pp 38-39.

Jaegermann, C. 1990. Effect of Water-Cement Ratio and Curing on Chloride Penetration into Concrete Exposed to Mediterranean Sea Climate. ACI Materials Journal, Vol 87, No 4, Jul-Aug, pp 333-339.

Johnston, C D. 1970. Strength and Deformation of Concrete in Uniaxial Tension and Compression. Magazine of Concrete Research, Vol 22, No 70, Mar, pp 5-16.

Jones, R and Kaplan, M F. 1957. The Effects of Coarse Aggregate on the Mode of Failure of Concrete in Compression and Flexure. Magazine of Concrete Research, Vol 9, No 26, pp 89-94.

Karavasiliadou, A. 1999. Role of Cement Content and Type on the Engineering and Durability Properties of Concrete. MSc Thesis, University of Dundee, UK.

Keene, P W. 1960. Some Tests on the Durability of Concrete Mixes of Similar Compressive Strength. Cement and Concrete association, Technical Report 330, Jan, 18pp.

Kumar, A, Roy, D M and Higgins, D D. 1987. Diffusion through Concrete. Concrete, Vol 21, No 1, Jan, pp 31-32.

Kumar, S and Rao, C V S K. 1995. Sulfate Attack on Concrete in Simulated Cast-In Situ and Precast Situation. Cement and Concrete Research, Vol 25, No 1, pp 1-8.

Larrard, F D. 1989. Ultrafine Particles for the Making of Very High Strength Concretes. Cement and Concrete Research, Vol 19, pp 161-172.

Lawrence, C D. 1990. The Mechanism of Corrosion of Reinforcement Steel in Concrete Structures, British Cement Association, Publication C8, 74pp.

Leng, F, Feng, N and Lu, X. 2000. An Experimental Study on the Properties of Resistance to Diffusion of Chloride Ions of Fly Ash and Blast Furnace Slag Concrete. Cement and Concrete Research, Vol 30, No 6, pp 989-992.

L'Hermite, R. 1960. Volume Changes of Concrete. Proceedings of 4th International Symposium on the Chemistry of Cement, Washington DC, USA, pp 659-694.

Li, C Q. 2000. Corrosion Initiation of Reinforcing Steel in Concrete under Natural Salt Spray and Service Loading - Results and Analysis. ACI Materials Journal, Vol 97, No 6, Nov-Dec, pp 690-697.

Li, C Q. 2001. Initiation of Chloride-Induced Reinforcement Corrosion in Concrete Structural Members - Experimentation. ACI Structural Journal, Vol 98, No 4, Jul-Aug, pp 502-510.

Limbachyia, M C. 1999. Current Perceptions of Concrete Admixtures. Concrete, Vol 33, No 10, Nov-Dec, pp 31-33.

Loo, Y H, Chin, M S, Tam, C T and Ong, K C G. 1994. A Carbonation Prediction Model for Accelerated Carbonation Testing of Concrete. Magazine of Concrete Research, Vol 46, No 168, pp 191-200.

Malhotra, V M. 2000. Role of Supplementary Cementing Materials in Reducing Greenhouse Gas Emissions. In: Concrete Technology for a Sustainable Development in the 21st Century, Edited by O E Gjφrv and K Sakai. E & FN Spon, London, UK, pp 226-235.

Mangat, P S and Molloy, B T. 1991. Influence of PFA, Slag and Microsilica on Chloride Induced Corrosion of Reinforcement in Concrete. Cement and Concrete Research, Vol 21, pp 819-834.

Mangat, P S and Molloy, B T. 1992. Factors Influencing Chloride-Induced Corrosion of Reinforcement in Concrete. Materials and Structures, Vol 25, pp 404-411.

Mangat, P S and Molloy, B T. 1994a. Prediction of Long Term Chloride Concentration in Concrete. Materials and Structures, Vol 27, pp 338-346.

Mangat, P S and Molloy, B T. 1994b. Prediction of Free Chloride Concentration in Concrete Using Routine Inspection Data. Magazine of Concrete Research, Vol 46, No 169, pp 279-287.

Mangat, P S and Molloy, B T. 1995. Chloride Binding in Concrete Containing PFA, GGBS or Silica Fume under Sea Water Exposure. Magazine of Concrete Research, Vol 47, No 171, pp 129-141.

Marsh, B. 1993a. A Summary of European Concreting Practice. Occasional Paper OP 53, Building Research Establishment, Garston, 115pp.

Marsh, B K. 1993b. European Concreting Practice: A Summary. Building Research Establishment Information Paper IP6/93, Garston, 4pp.

Maslehuddin, M, Saricimen, H and Al-Mana, A I. 1987. Effect of Fly Ash Addition on the Corrosion Resisting Characteristics of Concrete. ACI Materials Journal, Vol 84, No 1, Jan-Feb, pp 42-50.

Maslehuddin, M, Page, C L, Rasheeduzzafar and Al-Mana, A I. 1996. Effect of Temperature on Pore Solution Chemistry and Reinforcement Corrosion in Contaminated Concrete. In: Corrosion of Reinforcement in Concrete Construction, Edited by C L Page, P B Bamforth and J W Figg. Proceedings of the 4th International Symposium, Cambridge, UK, July, pp 67-75.

Maso, J C. 1996. Interfacial Transition Zone in Concrete. E & FN Spon, London, UK, 179pp.

Masterton, L. 1999. The Role of Cement Content in the Specification for Durability of Concrete. MSc Thesis, University of Dundee, UK.

McCarter, W J, Ezirim, H and Emerson, M. 1992. Absorption of Water and Chloride into Concrete. Magazine of Concrete Research, Vol 44, No 158, Mar, pp 31-37.

McCarthy, M J. 1991. Chloride and Carbonation-Induced Reinforcement Corrosion of PFA Concrete. PhD Thesis, University of Dundee, UK, 285pp.

McCarthy, M J, Dhir, R K and Jones, M R. 1996. Experiments on the Effect of Binder Type, Content and Air-Entrainment on Chloride Ingress in Concrete. In: Concrete in the Service of Mankind - Concrete for Infrastructure and Utilities, Edited by R K Dhir and N A Henderson. Proceedings of the International Conference, University of Dundee, UK, Jun, pp 29-38.

McCarthy, M J, Giannakou, A and Jones, M R. 2001. Specifying Concrete for Chloride Environments Using Controlled Permeability Formwork. Materials and Structures, Vol 34, Nov, pp 566-576.

Mehta, P K. 1980. Durability of Concrete in Marine Environment-A Review: Performance of Concrete in Marine Environment. ACI SP - 65, American Concrete Institute, Detroit, USA, pp 1-20.

Mehta, P K. 1991. Concrete in the Marine Environment. Elsevier Applied Science, Barking, England, 214pp.

Menzies, S A. 2002. Influence of Cement Content and Type on Concrete Mix Limitations for Durability. MSc Thesis, University of Dundee, UK, 333pp.

Meyer, A. 1968. Investigations on the Carbonation of Concrete. Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, pp 394-401.

Millard, S G. 1991. Reinforced Concrete Resistivity Measurement Techniques. Proceedings of the Institution of Civil Engineers, Part 2, Vol 91, Mar, pp 71-88.

Mills, R. 1987. Mass Transfer of Gas and Water through Concrete. In: Concrete Durability, Edited by J M Scanlon. ACI SP - 100, Vol 1, American Concrete Institute, Detroit, USA, pp 621-644.

Monteiro, P J M and Mehta, P K. 1986. Interaction between Carbonation Rock and Cement Paste. Cement and Concrete Research, Vol 16, pp 127-134.

Monteiro, P J M, Helene, P R L and Kang, S H. 1993. Designing Concrete Mixtures for Strength, Elastic Modulus and Fracture Energy. Materials and Structures, Vol 26, No 162, pp 443-452.

Munday, J G L. 1977. Influence of Loading History on Strength and Deformation of Plain Concrete. PhD Thesis, University of Dundee, UK.

Neville, A M. 1962. Shrinkage and Creep in Concrete. Structural Concrete, Vol 1, No 2, Mar-Apr, pp 49-85.

Neville, A M. 1995. Properties of Concrete – Fourth Edition. Pearson Education Limited, Essex, England, 844pp.

Ohno, Y, Praparntanatorn, S and Suzuki, K. 1996. Influence of Cracking and Water Cement Ratio on Macrocell Corrosion of Steel in Concrete. In: Corrosion of Reinforcement in Concrete Construction, Edited by C L Page, P B Bamforth and J W Figg. Proceedings of the 4th International Symposium, Cambridge, UK, July, pp 24-32.

Oluokun, F A. 1991. Prediction of Concrete Tensile Strength from Its Compressive Strength: Evaluation of Existing Relations for Normal Weight Concrete. ACI Materials Journal, Vol 88, No 3, pp 302-309.

Page, C L. 1975. Mechanisms of Corrosion Protection in Reinforced Concrete Marine Structures. Nature, Vol 258, No 5535, pp 514-515.

Page, C L, Short, N R and El Taraas, A. 1981. Diffusion of Chloride Ions in Hardened Cement Pastes. Cement and Concrete Research, Vol 11, No 3, pp 395-406.

Page, C L and Treadaway, K W J. 1982. Aspects of the Electrochemistry of Steel in Concrete. Nature, Vol 297, 13 May, pp 109-114.

Page, C L. 1985. Corrosion and Protection of Reinforcing Steel in Concrete. 13th Convention, Institute of Concrete Technology, Loughborough.

Page, C L and Havdahl, J. 1985. Electrochemical Monitoring of Corrosion of Steel in Microsilica Cement Pastes. Materials and Structures, Vol 18, No 103, pp 41-47.

Page, C L, Short, N R and Holden, W R. 1986. The Influence of Different Cements on Chloride-Induced Corrosion of Reinforcing Steel. Cement and Concrete Research, Vol 16, pp 79-86.

Page, C L. 1988. Introduction. In: Corrosion of Steel in Concrete, Edited by P Schiessl. RILEM Report of the Technical Committee 60-CSC, 102pp.

Parrott, L J. 1987. A Review of Carbonation in Reinforced Concrete - A Review Carried Out by C & CA under a BRE Contract. British Cement Association.

Parrott, L J. 1994. A Study of Carbonation-Induced Corrosion. Magazine of Concrete Research, Vol 46, No 166, Mar, pp 23-28.

Parrott, L J. 1996. Some Effects of Cement and Curing upon Carbonation and Reinforcement Corrosion in Concrete. Materials and Structures, Vol 29, pp 164-173.

Pettersson, K H. 1996. Factors Influencing Chloride Induced Corrosion of Reinforcement in Concrete. In: Durability of Building Materials and Components, Edited by C Sjostrom. Vol 1, Chapman and Hall, London, UK, pp 334-341.

Pourbaix, M. 1976. Atlas of Electrochemical Equilibrium in Aqueous Solutions. Pergamon Press, London, UK, 341pp.

Raphael, J M. 1984. Tensile Strength of Concrete. ACI Materials Journal, Vol 81, No 2, pp 158-165.

Raphael, M and Shalon, R. 1971. A Study of the Influence of Climate on Corrosion of Reinforcement. Concrete and Reinforcement Corrosion in Hot Countries, Vol VI, pp 77-96.

Rasheeduzzafar, Al-Mana, A, Haneef, M and Maslehuddin, M. 1986. Effect of Cement Replacement, Content and Type on the Durability Performance of Fly Ash Concrete in the Middle East. Cement, Concrete and Aggregates, Vol 8, No 2, pp 86-96.

Rasheeduzzafar, Dakhil, F and Mukarram, K. 1987. Influence of Cement Composition and Content on the Corrosion Behaviour of Reinforcing Steel in Concrete. In: Concrete Durability, Edited by J M Scanlon. ACI SP - 100, Vol 2, Apr, American Concrete Institute, Detroit, USA, pp 1477-1502.

Richardson, M G. 1988. Carbonation of Reinforced Concrete – Its Causes and Managements, CITIS Limited, 205pp.

Roy, D M and Idorn, G M. 1983. Hydration, Structure, and Properties of Blast-Furnace Slag Cements, Mortars, and Concrete. Journal of the American Concrete Institute, Proceedings Vol 79, No 6, Nov-Dec, pp 445-457.

Saeki, N, Takada, N and Fujita, Y. 1984. Influence of Carbonation and Sea Water on Corrosion of Steel in Concrete. Japanese Concrete Institution, Vol 6, pp 155-162.

Schiessl, P. 1975. Admissible Crack Width in Reinforced Concrete Structures. In: Inter-Association Colloquium on the Behaviour of In-Service Concrete Structures, Contribution No II, Preliminary Report Vol II, Liege, pp 3-17.

Schiessl, P and Breit, W. 1996. Local Repair Measures at Concrete Structures Damaged by Reinforcement Corrosion – Aspects of Durability. In: Corrosion of Reinforcement in Concrete Construction, Edited by C L Page, P B Bamforth and J W Figg. Proceedings of the 4th International Symposium, Cambridge, UK, July, pp 525-534.

Schiessl, P and Raupach, M. 1997. Laboratory Studies and Calculations on the Influence of Crack Width on Chloride-Induced Corrosion of Steel in Concrete. ACI Materials Journal, Vol 94, No 1, Jan-Feb, pp 56-62.

Shoya, M. 1979. Drying Shrinkage and Moisture Loss of Superplasticizer Admixed Concrete of Low Water Cement Ratio. Transactions of the Japan Concrete Institute, II-5, pp 103-110.

Singh, B G. 1958. Specific Surface of Aggregates Related to Compressive and Flexural Strength of Concrete. Journal of the American Concrete Institute, Proceedings Vol 54, Apr, pp 897-907.

Soroka, I and Setter, N. 1977. The Effect of Fillers on Strength of Cement Mortars. Cement and Concrete Research, Vol 7, No 4, pp 449-456.

Stewart, M G and Rosowsky, D V. 1997. Corrosion, Deterioration and Time-Dependent Reliability of Reinforced Concrete Bridge Decks. Structural Engineering Research Report, Clemson University, USA.

Stock, A F, Hannant, D J and Williams, R I T. 1979. The Effect of Aggregate Concentration upon the Strength and Modulus of Elasticity of Concrete. Magazine of Concrete Research, Vol 31, No 109, pp 225-234.

Subramanian, S. 1999. Interfaces in Concrete–Achieving Performance. In: Role of Interfaces in Concrete, Edited by R K Dhir and P C Hewlett. Proceedings of the International Seminar, University of Dundee, UK, Sep, pp 97-109.

Suzuki, K, Ohno, Y and Praparntanatorn, S. 1990. Mechanism of Steel in Cracked Concrete. In: Corrosion of Reinforcement in Concrete. 3rd International Symposium, Society of Chemical Industry.

Tanahashi, I, Ohgishi, S, Ono, H and Mizutani, K. 1987. Evaluation of Durability for Concrete In Terms of Watertightness by "Permeability Coefficient Test Results". In: Concrete Durability, Edited by J M Scanlon. ACI SP - 100, Vol 1, American Concrete Institute, Detroit, USA, pp 187-206.

Tasang, W A, Cripps, J C and Lynsdale, C J. 1998. Aggregate-Cement Chemical Interactions. Cement and Concrete Research, Vol 28, No 7, pp 1037-1048.

Teychenne, D C, Franklin, R E, Erntroy, H C and Marsh, B K. 1997. Design of Normal Concrete Mixes - Second Edition. Building Research Establishment, Watford, UK, 43pp.

Tham, K W. 1984. Superplasticized Normal - Workability Concrete: A Study of Its Properties in the Fresh and Hardened States. PhD Thesis, University of Dundee, UK.

Thaumasite Expert Group, 1999. Thaumasite Form of Sulfate Attack. Concrete, Vol 23, No 2, Feb, pp 37-40.

Thomas, M. 1996. Chloride Thresholds in Marine Concrete. Cement and Concrete Research, Vol 26, No 4, pp 513-519.

Thomas, M D A, Matthews, J D and Haynes, C A. 1990. Chloride Diffusion and Reinforcement Corrosion in Marine Exposed Concrete Containing PFA. In: Corrosion of Reinforcement in Concrete. Elsevier, Warwickshire, UK, pp 198-212.

Treadaway, K W J. 1988. Corrosion Period. In: Corrosion of Steel in Concrete, Edited by P Schiessl. RILEM Report of the Technical Committee 60-CSC, 102pp.

Tuutti, K. 1982. Corrosion of Steel in Concrete. Swedish Cement and Concrete Research Institute, S – 100 44, Stockholm, Sweden, 469pp.

Ward, M A. 1969. The Testing of Concrete Materials by Precisely Controlled Uniaxial Tension. PhD Thesis, University of London, UK.

Welch, G B. 1961. Discussion on Paper by H J Gilkey: Water-Cement Ratio Versus Strength - Another Look. Journal of the American Concrete Institute, Proceedings Vol 57, Part 2, Dec, pp 1866-1868.

Wilkins, N J M and Lawrence, P F. 1983. The Corrosion of Steel Reinforcements in Concrete Immersed in Seawater. In: Corrosion of Reinforcement in Concrete Construction, Edited by A P Crane. Ellis Horwood, London, UK, pp 119-141.

Winslow, D N, Cohen, M D, Bentz, D P, Snyder, K A and Garboczi, E D, 1994. Percolation and Pore Structure in Mortars and Concrete. Cement and Concrete Research, Vol 24, No 1, pp 25-37.

Wittmann, F, Gebauer, J and Torrent, R. 1996. The Versatility of Concrete. In: Concrete in the Service of Mankind – Appropriate Concrete Technology, Edited by R K Dhir and M J McCarthy. Proceedings of the International Conference, University of Dundee, UK, Jun, pp 149-160.

Wright, P J F and McCubbin, A D. 1952. The Effect of Aggregate Type and Aggregate/Cement Ratio on the Compressive Strength of Concrete. Department of Scientific and Industrial Research - Road Research Laboratory, Note No RN/1819/PJFW.ADMcC, Sep, 19pp.

Zhang, M and Gjorv, O E. 1990. Pozzolanic Reactivity of Lightweight Aggregate. Cement and Concrete Research, Vol 20, pp 884-890.

Zhou, S. 2001. Role of Cement Content in Specifications for Durability of Concrete. PhD Thesis, University of Dundee, UK, 365pp.

APPENDIX A

EXPERIMENTAL DETAILS OF LITERATURE REVIEW

Table A.1 Experimental details of literature review

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Basheer *et al*, 1994 (*f* – assumed)	PC*	Basaltic aggregate and natural sand	All specimens water-cured (20°C) to 3 days then, stored in laboratory for 7 months. **Air permeability:** Slab, 300 x 600 x 50 mm. "Autoclam" used to measure air permeability (no details given). **Carbonation depth:** Slab, 230 x 215 x 75 mm. 20% CO_2 exposure, 20°C / 65% RH, for 2 weeks. Carbonation depth measured using phenolphthalein indicator solution. **Freeze / thaw resistance:** Slab, 230 x 215 x 75 mm. ASTM C666, Procedure B, resaturated before 304 cycles and weight loss expressed as a % of maximum weight.	Workability allowed to vary (no details given). Superplasticizer used with some mixes to ensure full compaction. No air content details given.
Bissonnette *et al*, 1999 (*f*)	PC#	Crushed limestone (10 mm maximum size) and granitic sand	**Drying shrinkage:** Prism, 50 x 50 x 400 mm. Water-cured (23°C) to 28 days. Approximately 540 days drying at 23°C / 48% RH.	Workability allowed to vary (20 to 175 mm slump). Superplasticizer used at w/c ratio 0.35.
Buenfeld and Okundi, 1998 (*f*)	(i)100% PC# (ii) 60% PC and 40% PFA# (iii) 25% PC and 75% GGBS#	Thames Valley natural gravel and sand	**Compressive strength:** Cube, 100 mm. Water-cured (20°C) to 28 days. **Water absorption and oxygen permeability:** Cylinder, 100 mm dia. x 250 mm. After demoulding, wrapped in plastic film and cured at 20°C for 58 days. Cut three 50 mm thick slices from the central section, conditioned for 25 weeks at 30°C / 50% RH and, then, reduced to 21°C for 25 days. Water absorption measured at set time intervals up to 5 days by placing specimens on a pad of filter paper in a covered tray containing distilled water to a level just below the top of the filter paper. **Carbonation depth:** Three 100 mm dia. x 50 mm thick slices as for the water absorption test, conditioned for 25 weeks at 30°C / 50% RH. 5% CO_2 exposure, 30°C / 50% RH, for 20 weeks. Carbonation depth measured using phenolphthalein indicator solution. **Coefficient of chloride diffusion:** Three 100 mm dia. x 50 mm thick slices as for the carbonation depth measurement. Sealed slices (except one flat face) immersed in 5 M NaCl at 40°C for 84 days. Diffusion coefficient calculated using total chloride content profiles from Fick's second law.	Workability allowed to vary (no details given).

f Variation in cement and water contents at fixed free w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Collins, 1950 (*t*)	--*	(i) Natural gravel and sand (ii) Crushed granite (coarse and fine) (iii) Crushed gravel and natural sand (iv) Crushed granite and natural sand	**Compressive strength:** Cube, Water-cured at 16.6°C to 28 days.	High ultimate strength concrete (pre-stress) – high fines content. Workability allowed to vary (compacting factor 0.57 to 0.91).
Dhir *et al*, 1987a (*f*)	PC#	Natural gravel (20 mm maximum size) and sand	All specimens water-cured at 20°C to 28 days. **Compressive strength:** Cube, 100 mm. **Initial surface absorption:** Cube, 150 mm. After curing, specimens oven-dried at 105°C to constant mass. 200 mm head of water applied to sealed area 5000 mm². **Carbonation depth:** Cube, 100 mm. Water-curing followed by 14 days in air, 20°C / 55% RH. Sealed with wax on 5 surfaces. 4.0% CO_2 exposure, 20°C / 55% RH, for 20 weeks. Carbonation depth measured using phenolphthalein indicator solution. **Coefficient of chloride diffusion:** 8 mm thick slice used in diffusion cells as per Page *et al* (1981). No cylinder size, curing details given. **Freeze / thaw resistance:** Prism, 80 x 80 x 300 mm. Freezing: air at –18°C for 4 hours. Thawing: water at +5°C for 4 hours. Specified failure criteria: cycles for linear expansion strain of 300 x 10^{-5}. Specified exposure criteria: linear expansion after 250 cycles.	Workability constant (75 mm nominal slump) through use of a superplasticizer. Air content increased in cement reduced mixes (due to superplasticizer).
Dhir *et al*, 1987b (*f*)	PC#	Natural gravel and sand	All specimens either (i) 28-day water-cured, 20°C or (ii) 4-day water-cured, 20°C then, air-cured, 20°C / 55% RH. **Compressive strength:** Cube, 100 mm. **Initial surface absorption:** As Dhir *et al* (1987a).	Workability allowed to vary (25 to 180 mm slump).
Dhir *et al*, 1989b (*f*)	PC#	Natural gravel and sand	**Compressive strength:** Cube, 100 mm. Water-cured at 20°C to 28 days. **Carbonation depth:** As Dhir *et al* (1987a) except curing either (i) Water, 20°C, to 28 days or (ii) Air, 20°C / 55% RH, to 28 days.	Workability allowed to vary (25 mm to collapse slump).

f Variation in cement and water contents at fixed free w/c ratio
t Variation in cement and water contents at fixed total w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*
-- Not stated by author (assumed PC)

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Dhir *et al*, 1991 (*f*)	PC#	Natural gravel and sand	**Compressive strength:** Cube, 100 mm. Water-cured at 20°C to 28 days. **Abrasion resistance:** Slab, 295 x 295 x 80 mm. Water-cured (20°C) to 28 days and, then, dried at 20°C / 55% RH for 21 days. Modified BCA abrasion apparatus (15-minute exposure to a rotating wheel).	Workability allowed to vary (25 mm to collapse slump).
Dhir *et al*, 1996 (*f*)	(i) 100% PC# (ii) PC and PFA#	Natural gravel and sand	All specimens water cured at 20°C to 28 days. **Compressive strength:** Cube, 100 mm. **Initial surface absorption:** As Dhir *et al* (1987a). **Coefficient of chloride diffusion:** Cylinder, 100 mm dia. x 300 mm. 25 mm thick slice sealed in two-compartment cell. Exposure one side to 5 M NaCl. Chloride coefficient calculated using solution to Fick's Law.	Workability constant (75 mm nominal slump) through use of a high-range water-reducer. PFA replacement varied between 26 and 35%.
Dias, 1993 (*f*)	PC#	River gravel and sand	All specimens water-cured (temp. not given) to 28 days. **Compressive strength:** Cylinder, 100 mm dia. x 100 mm. Cylinder strength converted to standard cylinder strength (h/d = 2.0) by conversion factor (x 0.87); further converted to 100 mm cube strength by conversion factor (÷ 0.80). **Sorptivity:** Cylinder, 100 mm dia. x 100 mm. Specimens dried at 30°C / 90% RH to constant mass, after curing. Sorptivity calculated from volume of water absorption (determined from mass change) over 49 hours into cast surface. **Chloride content:** Cylinder, 100 mm dia. x 100 mm. After curing, 14 days dried at 30°C / 90% RH. Sides of cylinder sealed. Cast surface exposed to 35g/l NaCl solution (soaked sponge) for 16 weeks. Average total chloride content of 25 mm slice from exposed face determined by volumetric method (BS 4551: 1980).	Workability allowed to vary (0 and 60 mm slump).
Erntroy and Shacklock, 1955 (*t*)	PC*	Thames Valley natural gravel and sand	**Compressive strength:** Cube, 100 mm. 7 days water-cured at 20°C.	High strength (pre-stress). Workability allowed to vary (0 to 100 mm nominal slump).
Hansen and Almudaiheem, 1987 (*f*)	PC*	Natural gravel (maximum size 15 mm) and sand	**Drying shrinkage:** Cylinder, 76.2 mm dia. x 152.4 mm. Water-cured to 30 days. Drying at 20°C / 50% RH. Strain values at 375 days, extrapolated to ultimate strains at 3 years.	No workability data given.

f Variation in cement and water contents at fixed free w/c ratio
t Variation in cement and water contents at fixed total w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Hobbs, 1972 (*f*)	PC*	Thames Valley flint gravel (2.4 to 19 mm)	**Compressive strength:** Cube, 150 mm. 28-day water-cured at 19°C.	Workability allowed to vary (0 to 55 mm nominal slump).
Hughes and Ash, 1968 (*f*)	PC#	(i) Limestone coarse (5 to 20 mm) and fine (ii) Basalt coarse and Thames Valley sand (iii) Basalt coarse and fine (iv) Granite coarse and fine	**Compressive strength:** Cube, 100 mm. 28-day air-cured at 18°C / 95-100% RH.	Workability allowed to vary (no data given).
Johnson, 1970 (*f*)	--*	Crushed Basalt	Specimens water-cured to 28 days. **Compressive strength:** Equivalent cube, 102 mm (prism, 204 or 306 mm long, cut from 610 mm long specimen after uniaxial tensile test). **Tensile strength:** Prism, 102 x 102 x 152 mm. Uniaxial tensile test. Load applied via a friction grip.	No workability data given.
Keene, 1960 (*t*)	PC*	Thames Valley natural gravel and sand	**Compressive strength:** Cube, 100 mm. Water-cured at 14 to 18°C for 28 days. **Drying shrinkage:** Prism, 76 x 76 x 255 mm. Water-cured (14-18°C) for about 1 year. Dried to constant length at 105°C. **Water absorption:** Cube, 102 mm. Water-cured (14-18°C) to 28 days and, then, dried at 105°C for 72 hours. Absorption measured after 10 minutes of immersion. **Sulfate resistance:** Cube, 100 mm. Water-cured (14-18°C) to 28 days and, then, dried in air (temperature and RH not given) for 21 days. Na_2SO_4 exposure (0.5% by mass of SO_3) for 12 months. **Freeze / thaw resistance:** Cube, 100 mm. Water-cured (14-18°C) to 28 days. Freezing: water at -27°C for 15 hours. Thawing: air, variable outdoor temperature and duration (typically, three freeze / thaw cycles per week). Specified failure criteria: cycles for 5% mass loss.	Workability allowed to vary (0 to 200 mm nominal slump). No air-content details given.

f Variation in cement and water contents at fixed free w/c ratio
t Variation in cement and water contents at fixed total w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*
-- Not stated by author (assumed PC)

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Kumar and Rao, 1995 (*f*)	PC*	Natural gravel (20 mm maximum size) and river sand	**Sulfate resistance:** Cube, 150 mm. Water-cured to 28 days. Na_2SO_4 exposure (5000 ppm SO_4^{2-}) for 90 days.	Workability allowed to vary (no data given).
Loo *et al*, 1994 (*f*)	PC#	Crushed granite (20 mm) and natural sand (Zone C of BS 882)	**Compressive strength:** Cube, 100 mm. Water-cured at 20°C for 28 days. **Carbonation coefficient:** Cylinder, 100 mm dia. x 200 mm. Water-cured (20°C) to 3 days. Stored at 28°C / 82% RH, for between 13 and 71 days. 7.0% CO_2 exposure, 30°C / 65% RH, for 7 weeks. Carbonation depth measured with phenolphthalein indicator solution. Carbonation coefficient calculated from slope of carbonation depth against square root of time.	Workability allowed to vary (0 to 100 mm nominal slump).
Mangat and Molloy, 1992 (*f* – assumed)	PC#	Crushed granite (10 mm) and natural sand (Zone 2 of BS 882: 1965). Coarse agg. to fine agg. ratio = 0.5.	**Chloride content and resistance to corrosion:** Prism, 100 x 100 x 370 mm (plain and r/f concrete for chloride content and corrosion, respectively). 12 mm dia., high yield steel bar with 10 mm cover and 300 mm exposed length. Air-cured to 14 days. Sealed on 5 surfaces. Simulated marine splash zone – 6 hrs spray with North Sea water, 6 hrs drying in air for 600 days. Determined acid-soluble chloride content at the level of rebar, half-cell potential (w.r.t. SCE) and corrosion rate (using polarization resistance method).	Workability allowed to vary (no data given).
Mangat and Molloy, 1994 (*f*)	PC#	Crushed granite (10 mm) and natural sand (Zone M of BS 882)	**Chloride content:** Prism, 100 x 100 x 500 mm. Air-cured to 14 days. Sealed on 5 surfaces. Simulated marine splash zone – 6 hrs spray with North Sea water (approximately 2000 mM/l), 6 hrs drying in air for 520 days. Free chloride content determined by chemical analysis of pore fluid expressed from concrete under high triaxial pressure; value at surface extrapolated from measurements at 5, 15, 25 and 35 mm from exposed face.	Workability allowed to vary (no data given). Unusually, coarse agg. to fine agg. ratio is approximately 0.5.
Mangat and Molloy, 1995 (*f*)	PC#	As Mangat and Molloy (1994)	**Compressive strength:** Cube, cured to 28 days (no details given). **Chloride content:** As Mangat and Molloy (1994), except exposure (immersion in sea water having chloride ion concentration 500 – 700 mM/l, up to 270 days). Bound chloride content measured at a depth of 25 mm from exposed face.	As Mangat and Molloy (1994).

f Variation in cement and water contents at fixed free w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Maslehuddin *et al*, 1987 (*f*)	(i)100% PC[#] (ii) 80% PC and 20% PFA (class F)[#]	Crushed limestone (19 mm maximum size) and dune sand with coarse aggregate to fine aggregate ratio 1.7 by weight	**Resistance to corrosion:** Prism, 65 x 100 x 300 mm. Bar size, 12 mm dia. Cover to steel, 25 mm. Water-cured to 28 days. Exposure, partial immersion in 5% NaCl solution up to 1000 days. Tests, (i) Half-cell potential using SCE (ii) Corrosion rate by polarisation resistance method.	Workability allowed to vary (no data given). No details of chloride contents given. Half-cell potential 270 mV w.r.t. SCE considered as the limit for active corrosion.
McCarter *et al*, 1992 (*f*)	PC[#]	Crushed gravel (20 mm) and natural sand (Zone M of BS 882)	**Compressive strength:** Cube, 100 mm. Water-cured for 28 days. **Sorptivity:** Cylinder, 300 mm dia. x 150 mm. Sides sealed with bituminous paint at 24 hours and stored under polythene. Cylinder cut in half at 7 days. Air-dried (21°C / 55% RH) to 28 days. Tested by placing in water, 10 mm above the cut face. Sorptivity calculated by plotting cumulative volume of absorbed water over 25 hours against square root of time.	Workability allowed to vary (no data given).
McCarthy *et al*, 1996 (*f*)	(i) 100% PC[#] (ii) 70% PC and 30% PFA[#] (approxim -ately)	Natural gravel (20 mm) and sand	**Compressive strength:** Cube, 100 mm. Water-cured at 20°C for 28 days. **Initial surface absorption:** As Dhir *et al* (1987a). **Coefficient of chloride diffusion:** As Dhir *et al* (1996), except curing either (i) Water, 20°C, to 28 days or (ii) Air, 20°C / 55% RH, to 28 days.	Workability constant (75 mm nominal slump) through use of a superplasticizer.
Mills, 1987 (*f*)	PC*	Crushed quartzite fine aggregate and gravel (5 to 10 mm)	**Air permeability:** Cylinder, 150 mm dia. x 300 mm. No data given about curing. Tested using 54 mm dia. x 52mm cores and Nitrogen gas. Air permeability measured at a range of moisture contents and interpolated to 30%, for a confining pressure of 10 N/mm².	Workability constant (6 seconds nominal VB time) through use of a superplasticizer.
Monteiro *et al*, 1993 (*f*)	PC[#]	River gravel (9.5 mm maximum size) and natural sand	All specimens cured in a fog room at 20°C / RH > 99% for 28 days. **Compressive strength:** Cylinder, 100 mm dia. x 200 mm. Cylinder compressive strength converted to equivalent 100 mm cube strength by conversion factor (÷ 0.8). **Tensile strength:** Cylinder, 100 mm dia. x 200 mm. **Modulus of elasticity:** Cylinder, 100 mm dia. x 200 mm. Determined according to ASTM C 469.	Workability allowed to vary (< 10 to 200 mm slump).

f Variation in cement and water contents at fixed free w/c ratio
[#] Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Neville, 1962 (*t* - assumed)	--*	--	**Drying shrinkage:** Prism, cross section 127 x 127 mm. Specimens stored at 21°C / 50% RH for 6 months. Both mortar and concrete specimens used.	No workability data given.
Rasheeduzzafar *et al*, 1986 (*f*)	(i)100% PC# (ii) 70% PC and 30% PFA#	Crushed limestone and dune (beach) sand.	**Compressive strength:** Cylinder, 75 mm dia. x 150 mm. Water-cured at 20°C for 28 days. Cylinder compressive strength converted to equivalent 100 mm cube strength by conversion factor (÷ 0.8).	Workability allowed to vary (no data given).
Rasheeduzzafar *et al*, 1987 (*f*)	PC#	Crushed limestone (19 mm maximum size) and beach sand with coarse aggregate to fine aggregate ratio 2.0 by weight	**Resistance to corrosion:** Prisms, 62.5 x 100 x 300 mm. Bar size, 12.5 mm dia. Cover to steel, 25 mm. Water-cured to 28 days. Exposure, partial immersion in 5% NaCl solution up to 500 days at 23 to 25°C. Corrosion monitored using half-cell potential measured w.r.t. SCE.	Workability allowed to vary (no data given). No details of chloride contents given. Half-cell potential 270 mV w.r.t. SCE, considered as the limit for active corrosion.
Shoya, 1979 (*f* – assumed)	PC#	Andesite crushed stone (15 mm maximum size) and river sand	**Drying shrinkage:** Prism, 100 x 100 x 400 mm. Water-cured to 28 days. Dried in air at 20°C / 50% RH for 450 days. The Author interpolated from raw data to get values at equal w/c ratio.	No workability data given. Superplasticizer used for some mixes.
Singh, 1958 (*t*)	--*	Natural gravel and sand	**Compressive strength:** Cube, 100 mm. 7 days water-cured.	Workability allowed to vary (no data given).
Stock *et al*, 1979 (*f*)	--*	Natural gravel (150 μm to 19 mm)	Test age and curing details not stated. **Compressive strength:** Cylinder, 100 mm dia. x 300 mm. Cylinder compressive strength converted to equivalent 100 mm cube strength by conversion factor (÷ 0.8). **Tensile strength:** Specimen size not stated. Uniaxial tensile test. Load applied via a friction grip. **Modulus of elasticity:** Specimen size not stated. Modulus determined from the secant to 33% of the ultimate stress in compression from stress / strain plot to failure.	Workability allowed to vary (no data given).
Tanahashi *et al*, 1987 (*f*)	PC#	Natural gravel and sand	**Water permeability:** Disc, 150 mm dia. x 40 mm. Water-cured to 28 days. Oven dried at 60°C to constant mass for 3 days. Permeability coefficient calculated by applying a water pressure of 2.45 N/mm² for 30 minutes.	Workability allowed to vary (0 to 215 mm slump), water reducing admixture used in all mixes.

f Variation in cement and water contents at fixed free w/c ratio
t Variation in cement and water contents at fixed total w/c ratio
 # Cement contents stated in reference
**Cement contents calculated / estimated from mix details given in reference*
-- Not stated by author (assumed PC for cement type)

Table A.1 Experimental details of literature review (continued)

AUTHOR	CEMENT	AGGREGATE	PROPERTY AND TEST DETAILS	OTHER DETAILS
Ward, 1969 (*f*)	--*	Thames Valley gravel	**Tensile strength:** Specimen size, test age and curing details not stated. Uniaxial tensile strengths.	No workability data given.
Welch, 1961 (*f*)	RHPC*	Irregular river gravel and sand	**Compressive strength:** Cylinder, assumed 150 mm dia. x 300 mm. Tested at 7 days. Curing details not stated. Cylinder compressive strength converted to equivalent 100 mm cube strength by conversion factor (÷ 0.8).	High early strength concrete. Workability allowed to vary (0 to 90 mm).
Wright and McCubbin, 1952 (*t*)	--*	--	**Compressive strength:** Cube, tested at the age of 28 days. Curing details are not given.	Workability allowed to vary (no data given).

f Variation in cement and water contents at fixed free w/c ratio
t Variation in cement and water contents at fixed total w/c ratio
**Cement contents calculated / estimated from mix details given in reference*
-- Not stated by author (assumed PC for cement type)

APPENDIX B

EXAMPLES OF CONCRETE MIX DESIGN

PC, 42.5 / DOLOMITIC MAGNESIUM LIMESTONE AND NATURAL SAND: MIX No. __M1__

MAIN PARAMETERS

W/C ratio	=	__0.55__
Water content	=	__185___ kg/m³
Nominal slump	=	___75___ mm
Coarse aggregate type	=	uncrushed, 20 mm maximum size
% < 600μm of sand	=	___80___ %

CEMENT CONTENT (Clause 5.3 of BRE design method (Teychenne *et al*, 1997))

Cement content = water content / w/c ratio
= ___185__ / __0.55__ = ___336__ kg/m³ → ___335__ kg/m³

TOTAL AGGREGATE CONTENT (Clause 5.4, Figure 5)

For water content = ___185__ kg/m³
and 2.61 relative density for combined aggregates (assuming total aggregate contains 30% sand and 70% coarse aggregate), gives estimated wet density of concrete
= ___2375_ kg/m³

Total aggregate content = wet concrete density – cement content – water content
= __2375__ - __335___ - __185___ = __1855_ kg/m³

SAND CONTENT (Clause 5.5, Figure 6)

For 20 mm maximum aggregate size and 75 mm nominal slump,
with w/c ratio __0.55__ and ___80___ % sand < 600 μm, proportion of sand
= ___30___ %
(interpolated between data for 30 to 60 mm and 60 to 180 mm slump)

Sand content = total aggregate content x (proportion of sand / 100)
= __1855__ x (__30____ / 100)
= __557___ kg/m³ → ___555__ kg/m³

COARSE AGGREGATE CONTENT

Coarse aggregate content = total aggregate content – sand content
= __1855__ - __555___ → __1300__ kg/m³

After determining the mix proportions using the BRE method, the following procedure was applied:

- Correction for concrete yield based on the particle densities (at SSD for aggregates) of the mix constituents with no allowance made for entrapped air (therefore, slight over-yield).
- Calculation of batch quantities (with water content increased and aggregate content reduced) to allow for water absorption by the aggregate from laboratory dry to SSD.
- Measurement of plastic density as an approximate check on mix design and batching.

PC, 42.5 / DOLOMITIC MAGNESIUM LIMESTONE AND NATURAL SAND: MIX No. __M2__

MAIN PARAMETERS

W/C ratio	=	__0.55__
Water content	=	__165___ kg/m³
Nominal slump	=	___75___ mm
Coarse aggregate type	=	uncrushed, 20 mm maximum size
% < 600µm of sand	=	___80___ %

CEMENT CONTENT (Clause 5.3 of BRE design method (Teychenne *et al*, 1997))

Cement content = water content / w/c ratio
= ___165__ / __0.55__ = ___300__ kg/m³ → ___300__ kg/m³

TOTAL AGGREGATE CONTENT (Clause 5.4, Figure 5)

For water content = ___165__ kg/m³
and 2.61 relative density for combined aggregates (assuming total aggregate contains 30% sand and 70% coarse aggregate), gives estimated wet density of concrete
= ___2400_ kg/m³

Total aggregate content = wet concrete density – cement content – water content
= __2400__ - __300___ - __165___ = __1935_ kg/m³

SAND CONTENT (Clause 5.5, Figure 6)

For 20 mm maximum aggregate size and 75 mm nominal slump,
with w/c ratio __0.55__ and ___80___ % sand < 600 µm, proportion of sand
= ___30___ %
(interpolated between data for 30 to 60 mm and 60 to 180 mm slump)

Sand content = total aggregate content x (proportion of sand / 100)
= __1935__ x (__30____ / 100)
= __581___ kg/m³ → ___580__ kg/m³

COARSE AGGREGATE CONTENT

Coarse aggregate content = total aggregate content – sand content
= __1935__ - __580___ → __1355__ kg/m³

PC, 42.5 / DOLOMITIC MAGNESIUM LIMESTONE AND NATURAL SAND: MIX No. __M2*f*__

Mix proportions as above (M2), except the filler added to maintain the fines content equal to that of the Reference Mix (M1)

Fines content of M1 = cement content + 1 / 100 x sand content
= __335__ + __555__ / 100
= __340__ kg/m³

Fines content of M2 = __300__ + __580__ / 100
= __305__ kg/m³

Quantity of filler required for M2*f* = __340__ – __305__
= __35__ kg/m³

Adjusting sand to maintain yield, gives sand content for M2*f*
= __580__ – __35__
= __545__ kg/m³

END

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